Diastereoselective Access to 3-Nitro-4-vinylidenetetrahydrofurans and 3-Nitro-4-vinylidenetetrahydropyrans and Their Conversion into 3,6-Dihydro-1,2-oxazines by Reverse Cope Elimination of Hydroxylamine Precursors

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A new approach to the synthesis of unsaturated nitro-allenyltetrahydrofurans **3** and -tetrahydropyrans **5** has been developed, involving oxa-Michael addition/S_N2' substitution of propargyl and homopropargyl alcohol derivatives **2a** and **4h** on nitroalkenes**1a**–**g**. Complete allylic 1,3-strain control during the cyclization accounts for the observed diastereoselectivity. Reduction of nitro compounds **3** and **5** with SmI_2 provided new α–allenylhydroxylamines **7** and **8**, which were easily isomerized into 3,6-dihydro-1,2-oxazines **9** and **10** by reverse Cope elimination.

Introduction

Tetrahydrofuran and tetrahydropyran rings are present in a number of biologically significant natural products[1] and the synthesis of oxygen-containing heterocycles bearing unsaturated substituents is of great interest for further transformations. Among these substituents, the allenyl functionality has received only a little attention.[2]

In a recent report,[3] we disclosed a diastereoselective synthesis of 3-vinylidenetetrahydrofurans, made possible by a tandem oxa-Michael addition/S_N2' substitution of 4-chlorobut-2-yn-1-ol with nitroalkenes.

In this article we present the extension of this reaction to the synthesis of tetrahydropyran analogs and a study of the diastereoselectivity of the overall process. The preparation of α-allenylhydroxylamine precursors of 3,6-dihydro-1,2-oxazines by reverse Cope elimination[4] is also presented, with full experimental data.

Nitroalkenes constitute products of particular interest in synthesis, as many recent works testify, in terms either of their reactivity or their applications as key intermediates in the construction of complex molecules.[5] The powerfully electron-withdrawing effect of the nitro substituent is the main feature of nitroalkenes, which are hard electrophiles and therefore good acceptors in Michael additions[6] and efficient dienophiles in Diels−Alder reactions.[7]

The synthetic utility of these derivatives also arises from the easy transformation of nitro groups into many other functionalities, such as carbonyl functions,[8] hydroxylamines,[9] and amines,[10] or their complete reduction;[11] they are also precursors of the very reactive 1,3-dipolar reagents nitrile oxides and nitrones.[12]

Carbon nucleophiles such as enolates,[13] enamines,[14] trialkylaluminium,[15] allylsilanes,[16] and stannanes[17] have all been used in Michael additions with nitroalkenes for high yield formation of C−C bonds. Moreover, efficient synthesis of heterocycles have been furnished by the use of heteroanions: phosphorus, oxygen, nitrogen or sulfur.[5,18]

Works devoted to the synthesis of polyfunctionalized tetrahydrofurans and reported by Ono[19] and Chattopadhyaya[20] take advantage of a sequence involving successive Michael additions and radical carbocyclizations. Also of interest are intramolecular oxa- and aza-Michael additions to α-heterosubstituted nitroalkenes reported by Barrett,[21] which resulted in the formation of tetrahydrofurans and tetrahydropyrans. Recently, oxa-Michael-initiated tandem conjugate additions of 1-nitrocyclohexene to 4-hydroxybut-2-ynoates have been shown to afford alkylidenetetrahydrofurans.[22] A similar approach was involved in Pollini and Benetti's[23a] elegant diastereoselective synthesis of kaînoids for the construction of the properly functionalized pyrrolidine unit found in bioactive amino acids.

Nitronate anions, easily available from primary or secondary nitro groups, are good nucleophiles which readily add to α,β-unsaturated substrates or condense with carbonyl derivatives, through a Henry reaction. This strategy was extended to the synthesis of piperidine fragments, through the use of a homologue nucleophile in the aza-Michael addition.[23b] Finally, Hassner,[24] by addition of an allylic alcohol bearing an electron-withdrawing substituent, observed the formation of functionalized tetrahydrofurans. In these reports, cyclizations of nitronates resulting from the second conjugate addition in the oxa-Michael/Michael domino anionic sequence were 5-*exo*-*trig* in nature.

These results prompted us to investigate additions of 4-chlorobut-2-yn-1-ol to nitroalkenes; provided that the oxa-Michael addition is followed by S_N2' substitution, this tan-

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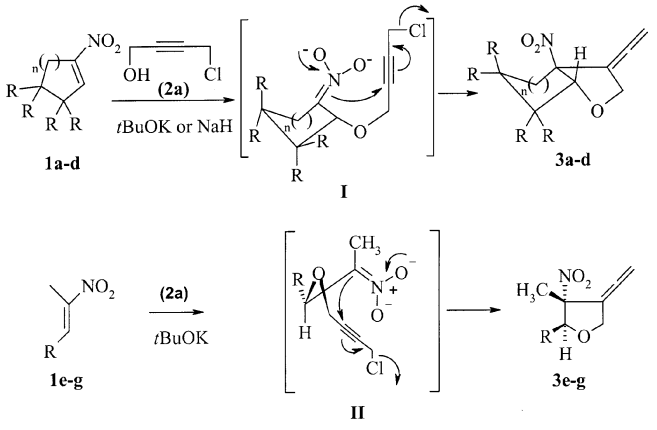
dem reaction should constitute a new route to vinylidenetetrahydrofurans.

Results

Many synthetic methods for the preparation of nitroalkenes have been reported.[5] Cyclic nitroalkenes **1a**−**d** were prepared in two steps from corresponding cycloalkenes by nitromercuration/elimination.[25] Nitroalkene acetal **1c** was isolated as a single regioisomer. The olefinic acetal precursor of **1d** was prepared according to a literature procedure.[26] Crude β-nitroalcohols were obtained by aldol condensation (Henry reaction) between nitroethane and benzaldehyde, acetaldehyde, or hexanal.[27] Acyclic nitroalkene **1f** resulted from dehydration with basic alumina in CH_2Cl_2 [28] while isolation of **1e** and **1g** first required formation of mesylates, which subsequently underwent Et_3N-promoted elimination.[29] The stereochemistries of the nitroalkenes were assigned on the basis of ^1H NMR spectra, by comparison with reported data.[30]

Nitroalkenes **1a**−**g** were treated with 4-chlorobut-2-yn-1-ol (**2a**)[31] at 0 °C in THF/*t*BuOH, in the presence of *t*BuOK (1.5 equiv.). After 10 min, the mixture was allowed to warm and maintained at room temperature until completion of reaction (10−30 min).

According to the known reactivity of nitroalkenes with oxygen nucleophiles, the oxa-Michael addition first affords nitronate **I**, which then undergoes S_N2' substitution to provide the allenyl moiety[32] (Scheme 1).

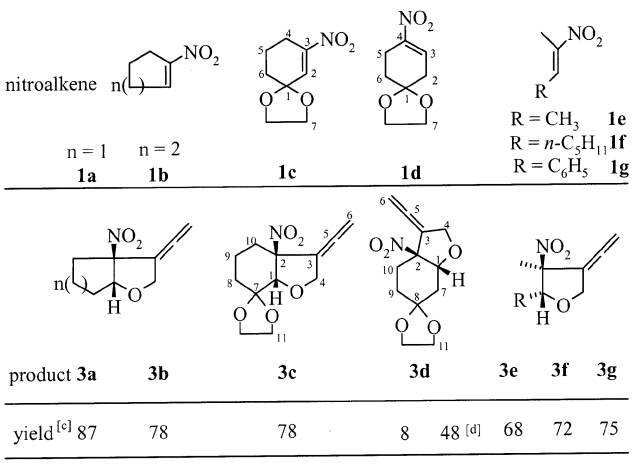


Scheme 1. Preparation of 3-nitro-4-vinylidene tetrahydrofurans **3a**−**g**.

Vinylidenetetrahydrofurans **3a**−**g** were isolated as the sole products, in 48−87% yield after flash chromatography on silica gel (Table 1).

The results given in Table 1 summarize the synthetic aspects of the procedure, with vinylidenetetrahydrofurans **3a**−**g** being obtained in good yield from α,β-disubstituted nitroalkenes. Under the same reaction conditions, nitroalkene **1d** afforded vinylidenetetrahydrofuran **3d** in low yield (8%), together with remaining starting material; this lower reactivity was attributed to the steric bulk of the ketal protective group, which prevents the approach of nucleophile to the vicinal carbon. More drastic conditions resulted in degradation. Finally, the use of NaH as the base in THF resulted in the formation of **3d** in 48% yield.

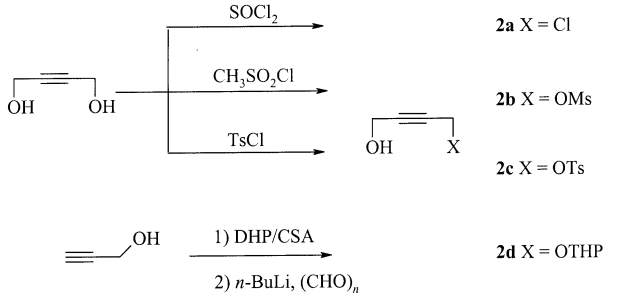
Table 1. Obtainment of 3-nitro-4-vinylidene tetrahydrofurans **3a**−**g**.



yield [c]	87	78	78	8	48 [d]	68	72	75

[a] Numbers refer to NMR assignments (see Exp. Section). − [b] Reaction conditions: **2a**, *t*BuOK (1.5 equiv.), THF, 0 °C − [c] Yields are given for isolated compounds − [d] Reaction conditions: **2a**, NaH (1.6 equiv.), THF, 0 °C.

A study of the influence of the propargylic leaving group on the nucleophile was undertaken with 1-nitrocyclohexene **1a** as a model compound. Alkylsulfonate leaving groups (mesylate **2b** and tosylate **2c**) were prepared according to known procedures,[33] while tetrahydropyranyl ether **2d** was obtained in two steps from propargyl alcohol (Scheme 2). With the poor OTHP leaving group, we only observed decomposition of nitroalkene.



Scheme 2. Preparation of propargyl alcohol derivatives **2a**−**d**.

The similar leaving group properties of X = OMs and OTs resulted in allenyltetrahydrofuran **3b** being obtained in 66 and 76% yields, respectively.

Bicyclic allenyltetrahydrofurans exhibit *cis* ring fusion, due to stereoelectronic effects during cyclization (Scheme 1). Interestingly, exclusively *trans* stereochemistry results from cyclization of acyclic (*E*)-nitroalkenes to give **3e**−**g**. We assume that the diastereoselectivity observed is due to 1,3-allylic strain,[34] which allows only one conformation (**II**) for the transition state, which gives rise to

the *trans* stereoselectivity observed in the intramolecular cyclization (Scheme 1).

After addition of nucleophile, the intermediate nitronate adopts a favored conformation in which the hydrogen at C1 and the nitronate are eclipsed; this conformation allows effects resulting from 1,3-allylic strain to be avoided. The consequence is total facial selectivity in the nitronate cyclization, which provides *trans* vinylidene tetrahydrofurans in a total stereoselective manner. Effects of 1,3-allylic strain have previously been invoked to account for high selectivities observed in nitronate-controlled kinetic protonation,[35] or intermolecular cycloaddition of nitrones in the presence of a chiral center adjacent to the π-system.[36]

The *trans* stereochemistry was assigned on the basis of NOESY experiments (Figure 1). Correlation between the hydrogens of the CH_3 and n-C_5H_{11} groups attested to a *cis* relationship between these substituents.

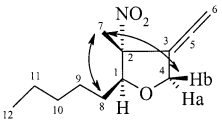
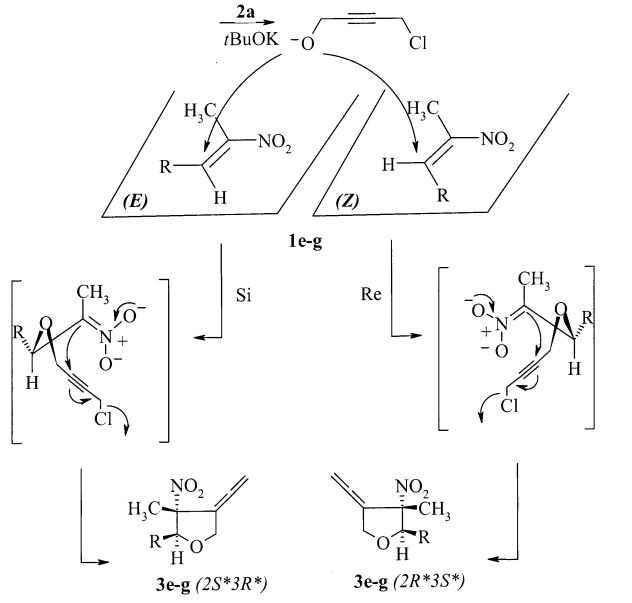


Figure 1. Stereochemistry of **3f** as assigned by NMR NOESY experiment.
[a] Numbers refer to NMR assignments (see Exp. Section).

A study of the diastereospecificity of the transformation required the preparation of *Z* nitroalkenes. Most of the available procedures for the synthesis of nitroalkenes are known to provide thermodynamically more stable *E* isomers, independently of the nitro compound precursors.[37] The stereochemistry of the double bond is easily assigned by ^{1}H NMR, since vinylic hydrogen is more deshielded in *E* isomers than in their *Z* counterparts, due to the anisotropic effect of nitro groups. Although a few *Z* nitroalkenes have been obtained by the stereospecific nitroselenylation procedure reported by Tomoda,[38] this method is limited to symmetric alkenes only, and there is no direct access to *Z* compounds available.

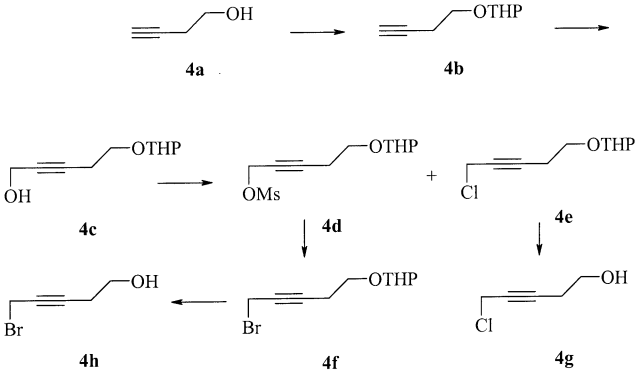
Nevertheless, it was possible to prepare (*Z*)-**1f** and (*Z*)-**1g** indirectly, from the respective *E* derivatives;[35d] indeed, when treated with selenolate anion, generated in situ, and subsequently kinetically protonated at −78 °C, (*E*)-**1f** and (*E*)-**1g** afforded 99:1 and 58:42 *R**/*S** mixtures of β-nitroethers, which selectively produced nitroalkenes (*Z*)-**1f** and (*Z*)-**1g**, respectively, after H_2O_2-promoted *syn* elimination. Thus, the sequential oxa-Michael addition/S_N2' substitution of 4-chlorobut-2-yn-1-ol has been performed under standard conditions with (*Z*)-**1f** and a *Z*/*E* mixture (1:0.7) of isomeric nitroalkenes **1g**. Comparison of the ^{1}H and ^{13}C NMR spectra of the resulting nitro-vinylidene tetrahydrofurans with those of **3f** and **3g** indicated that the same diastereomers were obtained, independently of the stereochemistries of the starting nitroalkenes.

A totally 1,3-allylic strain-controlled diastereoselective formation of 3-vinylidenetetrahydrofurans attests to the nondiastereospecificity of the transformation (Scheme 3).



Scheme 3. 1,3-Allylic strain control over diastereoselectivity in the formation of 3-nitro-4-vinylidene-tetrahydrofurans **3e**−**g**.

These results prompted us to extend the overall sequence to the synthesis of 3-nitro-4-vinylidenetetrahydropyrans. 5-Bromopent-3-yn-1-ol (**4h**), the required nucleophile for a potential six-membered ring cyclization to occur in the tandem reaction, was synthesized in five steps (38% yield) from commercially available but-3-yn-1-ol (**4a**) (Scheme 4).



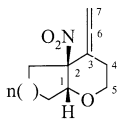
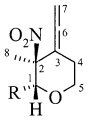
Scheme 4. Preparation of homopropargyl alcohol derivatives **4g** and **4h**.

Although longer reaction times were necessary for completion of the reaction, standard conditions as previously developed for the synthesis of 5-membered ring analogs allowed a general preparation of 3-nitro-4-vinylidenetetrahydropyrans **5** in good yields, with the exceptions of **1c** and **1d**, which remained unchanged under the reaction conditions. In the presence of an excess of base (3 equiv.), however, attempted transformation of **2c** and **2d** resulted in degradation.

5-Chloropent-3-yn-1-ol (**4g**), prepared from tetrahydropyranyl ether precursor **4e** (Scheme 4), was also tested as a promoting leaving group for the S_N2' substitution step;

we noticed that the use of chlorine, a less efficient leaving group resulted in a low yield formation of allenyltetrahydropyran **5b** (Table 2).

Table 2. Preparation of 3-nitro-4-vinylidenetetrahydropyrans by oxa-Michael addition/S_N2' substitution of nitroalkenes with 5-bromopent-3-yn-1-ol (**4h**)

nitroalkene	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**
							
	n =	n = 2			R = CH_3	n-C_5H_{11}	C_6H_5
product	**5a**	**5b**	_	_	**5e**	**5f**	**5g**
yield[b]	68	74	10[c]	_	68	83	75

[a] Numbers refer to NMR assignments (see Exp. Section) – [b] Yields are given for isolated compounds – [c] Yield obtained with 5-chloropent-3-yn-1-ol (**4g**)

As with allenyltetrahydrofurans **3a**–**d**, bicyclic pyran derivatives **5a** and **5b** feature *cis* ring fusion, while monocyclic compounds **5e**–**g** are selectively obtained in the *trans* forms. Totally 1,3-allylic strain-controlled diastereoselectivity could still account for the observed stereochemistry: facial selectivity during intramolecular cyclization of nitronate is totally dependent on oxa-Michael addition of nucleophile to nitroalkene. The *trans* stereochemistry was assigned for **5f** by NOESY homonuclear correlation, which indicated a *cis* relationship between alkyl substituents at C^1 and C^2. Moreover, correlation between H^1 and H^{5b} attested to their 1,3-diaxial arrangement; it was therefore possible to assign equatorial positions to the n-C_5H_{11} and nitro substituents (Figure 2). Condensation of 5-bromo-pent-3-yn-1ol (**4h**) with (*Z*)-2-nitro-2-octene (**1f**) resulted in the isolation of *trans*-**5f**, which again confirmed the nonstereospecificity of the sequence in the case of vinylidenetetrahydropyrans.

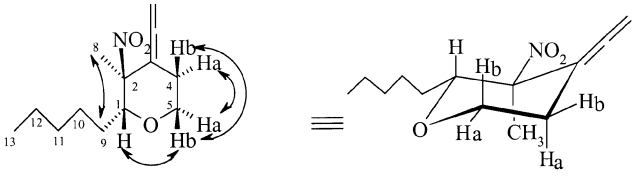
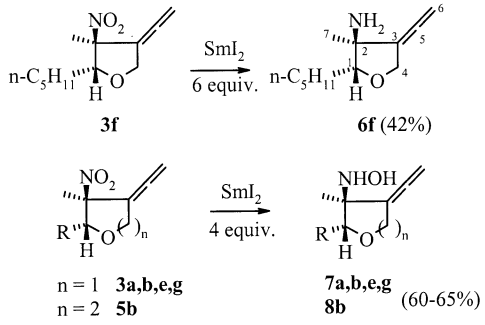


Figure 2. Stereochemistry of **5f** assigned by NOESY.
[a] Numbers refer to NMR assignments (see Exp. Section).

The oxa-Michael addition/S_N2' substitution sequence developed constitutes a quite general, efficient and stereocontrolled procedure for the preparation of vinylidenetetrahydrofurans and vinylidenetetrahydropyrans. Moreover, the ability of the nitro group to undergo transformations into various functionalities endows these compounds with promising synthetic potential.

Therefore, although a number of methods for the synthesis of allenic amines are available,[39] of those nitrogen derivatives with higher oxidation states, allenylhydroxylamines have never, to the best of our knowledge, been described. Reduction of nitro compounds has been used for a long time as a conventional method for the preparation of amines and hydroxylamines;[40] in the latter instance, however, overreduction can occur in many cases and further reduction to amines is difficult to avoid. Only a few preparative procedures report a controlled conversion of nitro compounds into hydroxylamines. Among these are Zn reduction under neutral conditions ($Zn/NH_4Cl/H_2O$)[41] and sodium borohydride-catalyzed borane reduction of nitroalkenes;[42] particularly reactive and chemoselective stannyl complexes have also been shown to provide alkylhydroxylamines through nitroso compounds and without any further reduction.[43] Since the previous work of Kagan et al on the reactivity of SmI_2 with nitrogen compounds,[44] alkylhydroxylamines and alkylamines have been selectively prepared from nitroalkanes and SmI_2 under mild conditions. Indeed, Kende et al.[45] reported that, in the presence of methanol as a proton source, nitro compounds could be converted into hydroxylamines with 4 equiv. SmI_2, while conversion into amines could be effected with 6 equiv. SmI_2 and longer reaction times.

According to this procedure, allenylamine **6f** was obtained in 42% yield by treatment of **3f** with 6 equiv. SmI_2 in THF/*t*BuOH (Scheme 5).

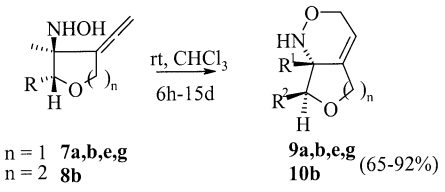


Scheme 5. Reduction of nitro allenes by SmI_2.
[a] Numbers in **6f** refer to NMR assignments (see Exp. Section).

Treatment of nitrovinylidenetetrahydrofurans **3a**, **3b**, **3e**, **3g** and nitrovinylidenetetrahydropyran **5b** with 4 equiv. 0.1 M SmI_2 over 15 min resulted in the isolation of the (crude) corresponding hydroxylamines **7a, 7b, 7e, 7g** and **8b** in 60–65% yields (Scheme 5), with fully satisfactory spectroscopic data. However, these materials were partially decomposed after flash chromatography on silica gel.

Upon standing for 6 h at 0 °C in $CDCl_3$ filtered through basic aluminum oxide (NMR tube), **7b** was unexpectedly transformed into 3,6-dihydro-1,2-oxazine **9b**, according to an overall formal 6-*endo O*-alkylation process (Scheme 6).

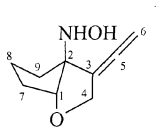
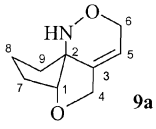
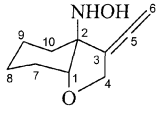
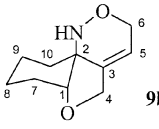
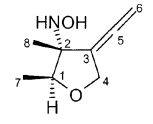
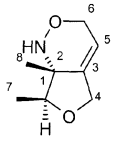
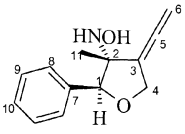
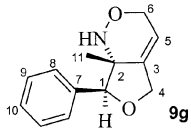
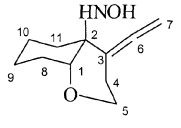
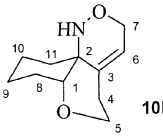
Indeed, the well documented electrophilically catalyzed intramolecular cyclizations of β-allenic alcohols into dihydropyrans[46] suggest that cyclic derivatives of hydroxylamines, namely 3,6-dihydro-1,2-oxazines, should be



Scheme 6. Formation of 3,6-dihydro-1,2-oxazines.

provided through analogous cyclizations of α-allenylhydroxylamines. This isomerization after standing at higher temperatures proved to be general, and 3,6-dihydro-1,2-oxazines **9b**, **9e**, and **9g** were cleanly obtained after 6−10 h at room temperature, in 72−80% yields, while conversion of **7a** was accomplished in 15 days (Table 3, entry 1). In this case, the transformation was slow, due to the strain implicit in the construction of the [5.5.6] tricyclic system in **9a**. Conversion of **7b** also proceeded smoothly and in high yield at −20 °C for 48 h; heating, on the other hand, resulted in the degradation of starting material (Table 3, entry 2). Moreover, **8b** provided tricyclic **10b** in good yield, although the transformation required 10 days at room temperature.

Table 3. Preparation of 3,6-dihydro-1,2-oxazines.

entry	hydroxylamine	reaction conditions	3,6-dihydro-1,2-oxazine	yield [%][b]
1		rt, 15d		65
2	**7a**	50°C, 40 min	**9a**	0
3		rt, 6h		73
4	**7b**	-20°C, 48h	**9b**	92
5		rt, 6h		72
	7e		**9e**	
6		rt, 10h		80
	7g		**9g**	
7		rt, 10d		71
	8b		**10b**	

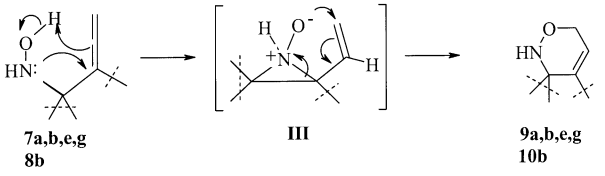
[a] Numbers refer to NMR assignments (see Exp. Section). – [b] Yields are given for isolated products.

Use of two-dimensional NMR techniques (HMBC and HMQC) for structural determination of **9b** unambiguously confirmed the structure of the oxazine system. This uncatalyzed intramolecular cyclization of hydroxylamines contrasts with the well-known electrophilically catalyzed process required for the cyclization of functionalized allenyl derivatives[46,47] Among these, BF_3/Et_2O- or Ag^I-catalyzed cyclizations of allenyl alcohols, amines, or oximes give rise to 5-membered or 6-membered heterocycles in good yields, with *exo-trig* or *endo-trig* regioselectivities observed, depending on substitution at the allene distal carbon, chain length, and the choice of catalyst. To date, 5-*endo-trig* cyclization of an α-allenyl amine derivative into 3-pyrroline at 210 °C constitutes a unique reported process in not being Lewis acid-catalyzed.[48]

In view of these literature reports, we assume that the spontaneous isomerization of hydroxylamines into dihydrooxazines, not requiring activating catalyst, rules out a 6-*endo-trig* regioselective cyclization promoted by initial direct addition of oxygen at the allene distal carbon. The fact that the cyclizations proceed uncatalyzed at ambient temperature might rather be accommodated by invoking a pathway that features a reverse Cope elimination.[49] According to a concerted *syn* elimination process, a five-membered transition state accounts for recently reported cyclizations of unsaturated hydroxylamines into nitrones[50a] and pyrrolidine *N*-oxides,[50b] or addition of oximes on alkenes[51] and alkynes.[52]

Of particular interest among these transformations is the synthesis of aza-heterocycles of the isoquinuclidine skeleton,[49,53] made possible by a promoted retro-Cope hydroxylamino oxime limonene derivative elimination, previously reported as an acid-catalyzed cyclization.[54]

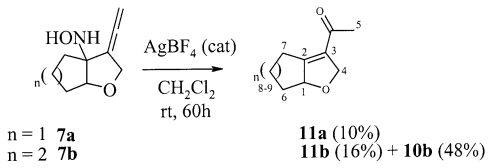
Transformation of allenylhydroxylamines **7** and **8** into oxazines **9** and **10** might proceed according to Scheme 7, which implies the transient formation of aziridine *N*-oxide **III** and subsequent scission and neutralization of the protonated 3-membered aza ring created by addition of oxygen at the vinylic moiety. Moreover, this pathway proceeds according to the conventional reactivity of hydroxylamines, which undergo alkylation on nitrogen rather than oxygen, by addition to the activated double bond.[55]



Scheme 7. Reverse Cope elimination of α-allenylhydroxylamines into 3,6-dihydro-1,2-oxazines.

In order to corroborate the hypothesis of a *retro*-Cope elimination mechanism, we decided to study the behavior of α-allenylhydroxylamines **7a** and **7b** in the presence of Lewis acids. After 60 h at room temperature, in the presence of catalytic amount of $AgBF_4$, **7a** and **7b** had been trans-

formed into 3-acyl-2,5-dihydrofurans **11a** and **11b** in 10 and 16% yields, respectively (Scheme 8).



Scheme 8. Formation of acetyldihydrofurans; numbers refer to NMR assignments (see Exp. Section)

Although **11a** constitutes the exclusive product of the transformation of **7a**, compound **7b**, under the same reaction conditions, afforded acetyl furan **11b**, along with **10b** as the major product. The longer time required for the formation of oxazine **9a** from **7a** makes this latter pathway uncompetitive with the production of acetyl furan **11a**, which is then isolated selectively.

Conclusion

In conclusion, this work reports efficient sequences of oxa-Michael additions, cyclizations, and reductions applied to nitroalkenes, providing a new route to elaborated heterocycles. More particularly, selective reduction of nitroallenes into the corresponding hydroxylamines upon treatment with SmI_2, and their remarkably facile cyclization into 3,6-dihydro-1,2-oxazines constitutes an alternative to the synthesis of these compounds; prior to our preliminary report,[4] despite their synthetic potential, 3,6-dihydro-1,2-oxazines had been prepared solely by [4+2] cycloaddition.[56] Indeed, our new rearrangement has recently been involved in an elegant enantioselective synthesis of oxazines by spontaneous conversion of chiral allenylhydroxylamines.[57] Since 3,6-dihydro-1,2-oxazines are involved in strategies devoted to the synthesis of indolizidine alkaloids,[58] due mainly to the easy cleavage of the N−O bond to generate 1,4-bifunctional groups,[59] our work should undergo interesting future development.

Experimental Section

General Remarks: ^1H and ^{13}C NMR were recorded on Bruker AC 200 or AMX 400 spectrometers. $CDCl_3$ was used as the solvent, unless otherwise specified. Chemical shifts are given in ppm (δ) downfield from residual, nondeuterated solvent ($CHCl_3$, δ = 7.24). − Mass spectra were performed on a Kratos MS 50 at 70 and 12 eV. − IR spectra were recorded in cm^{-1} on a Perkin−Elmer 1600 series FT-IR. Tetrahydrofuran (THF) was distilled from sodium and benzophenone (dark blue-purple color) under a N_2 atmosphere. − Flash column chromatography was performed on silica gel 60 (Merck 230−400 mesh), and TLC on precoated silica gel plates/UV_{254} (Macherey−Nagel).

Preparation of Cyclic Nitroalkenes (1a−d)[25b,25c]

1-Nitrocyclopentene (1a): Yield 69%. − R_f = 0.65 (diethyl ether/petroleum ether = 70:30). − IR: $\tilde{\nu}$ = 2922, 1651, 1558, 1542, 1092 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 2.11 (quint, J = 7.4 Hz, 2 H), 2.60 (m, 2 H), 2.83 (m, 2 H), 6.98 (quint, J = 2.0 Hz, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.9, 29.3, 30.8, 138.7, 153.1.

1-Nitrocyclohexene (1b): Yield 71%. − R_f = 0.64 (diethyl ether/petroleum ether = 70:30). − IR: $\tilde{\nu}$ = 2944, 2864, 1666, 1516, 1080 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.54−1.88 (m, 4 H), 2.32 (m, 2 H), 2.55 (m, 2 H), 7.30 (quint, J = 2.0 Hz, 1 H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 20.5, 21.6, 23.7, 24.6, 134.3, 149.5.

3-Nitrocyclohex-2-en-1-one Ethylene Acetal (1c): Yield 72%. − R_f = 0.60 (diethyl ether/petroleum ether = 70:30). − IR $\tilde{\nu}$ = 2976, 1530, 1005 cm^{-1}. − ^1H NMR (200 MHz, $CDCl_3$): δ = 1.85 (m, 4 H, H5,6), 2.58 (m, 2 H, H6), 4.05 (m, 4 H, H7), 6.88 (s, 1 H, H2). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.5, 23.7, 32.4 (C4), 64.9 (C7), 105.2 (C1), 129.6 (C2), 152.1 (C3). − $C_8H_{11}NO_4$ (185.18): calcd. C 51.89, H 5.99, N 7.56; found C 51.81, H 6.02, N 7.50.

4-Nitrocyclohex-3-en-1-one Ethylene Acetal (1d): Yield 70%. − R_f = 0.43 (diethyl ether/petroleum ether = 70:30). − IR: $\tilde{\nu}$ = 2923, 1650, 1525, 1381, 1098 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.86 (tt, J = 6.6 and 0.8 Hz, 2 H, H6), 2.51 (dtt, J = 4.2, 2.5 and 0.8 Hz, 2 H, H2), 2.78 (ttd, J = 6.7, 2.5 and 1.4 Hz, 2 H, H5), 3.97 (s, 4 H, H7), 7.15 (tt, J = 4.2 and 1.4 Hz, 1 H, H3). − ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 23.1 (C5), 30.5 (C6), 35.1 (C2), 64.8 (C7), 106.3 (C1), 131.4 (C3), 148.9 (C4). − $C_8H_{11}NO_4$ (185.18): calcd. C 51.89, H 5.99, N 7.56; found C 51.80, H 6.05, N 7.48.

General Procedure for the Preparation of Acyclic Nitroalkenes 1e−g: NaOH (10 N, 10 mL) was slowly added at 0 °C, with vigorous stirring, to a solution of nitroethane (7.2 mL, 0.1 mol) and aldehyde (0.1 mol acetaldehyde, hexanal, or benzaldehyde) in methanol (15 mL). After 12 h stirring at room temperature, the mixture was diluted with ice (10 mL) and neutralized with 5% HCl. After extraction with diethyl ether (3 × 25 mL), the combined extracts were dried over $MgSO_4$ and concentrated in vacuo to afford crude β-nitroalcohols.

Methanesulfonyl chloride (4 mmol, 310 μL) was added at 0 °C under argon to a solution of 2-nitro-3-hydroxybutane or 2-nitro-3-hydroxy-3-phenylpropane (4 mmol) in CH_2Cl_2 (4 mL). Et_3N (2.22 mL, 16 mmol, 4 equiv.) was added dropwise and the mixture was stirred at 0 °C for 1 h, then diluted with H_2O (10 mL). After extraction with diethyl ether (3 × 30 mL), the combined extracts were dried over $MgSO_4$, and concentrated in vacuo. Crude products were purified by chromatography on silica gel to provide nitroalkenes (*E*)-**1** and (*E*)-**1g**.

(*E*)-2-Nitro-but-2-ene (1e): Yield 69%. − R_f = 0.50% (diethyl ether/petroleum ether = 70:30). − IR: $\tilde{\nu}$ = 2961, 1651, 1543, 1095, 1034 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 1.86 (dq, J = 7.3 and 1.0 Hz), 2.13 (br. s, 3 H), 7.17 (br. q, J = 7.3 Hz, 1 H). − ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 12.1, 13.5, 131.5, 148.3. − $C_4H_7NO_2$ (101.11): calcd. C 47.52, H 6.98, N 13.85; found C 47.45, H 7.05, N 13.78.

(*E*)-(2-Nitroprop-2-en-1-yl)benzene (1g): Yield 88%. − R_f = 0.60 (diethyl ether/petroleum ether = 70:30). − IR: $\tilde{\nu}$ = 2924, 1651, 1552, 1393, 1181 cm^{-1}. − ^1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (br. s, 3 H), 7.42 (br. s, 5 H), 8.07 (br. s, 1 H). − ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 13.9, 128.8, 129.8, 129.9, 132.3, 133.4, 147.2. − $C_9H_9NO_2$ (163.18): calcd. C 66.25, H 5.56, N 8.58; found C 66.17, H 5.60, N 8.51.

(*E*)-2-Nitro-oct-2-ene (1f): A solution of 2-nitro-3-hydroxyoctane (0.5 mmol) in CH_2Cl_2 (6 mL) containing Al_2O_3 (1 g, reactivity I, Brockman), was refluxed for 20 h. The mixture was filtered through

Celite, the solvent was evaporated, and the residue was chromatographed on silica gel to afford **(*E*)-1f**: Yield 72%. – R_f = 0.73 (diethyl ether/petroleum ether = 70:30). – IR: $\tilde{\nu}$ = 2959, 2951, 2863, 1637, 1558, 1520, 1390, 1084 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 6.3 Hz, 3 H), 1.22–1.54 (m, 6 H), 2.14 (br. s, 3 H), 2.20 (q, *J* = 7.6 Hz, 2 H), 7.12 (t, *J* = 7.6 Hz, 1 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 12.4, 13.8, 22.3, 27.9, 28.0, 31.4, 136.4, 147.5. – $C_8H_{15}NO_2$ (157.21): calcd. C 61.12, H 9.62, N 8.91; found C 61.06, H 9.70, N 8.85.

General Procedure for the Preparation of (*Z*)-Nitroalkenes 1f and 1g: Diphenyl diselenide (122 mg, 0.39 mmol) was dissolved in absolute ethanol (2.5 mL). Sodium borohydride (30 mg, 0.79 mmol, 2 equiv.) was added in small portions, while stirring under nitrogen was maintained, at 0 °C, until the bright yellow solution turned colorless. **(*E*)-**nitroalkene **1f** or **1g** (0.65 mmol) in solution in EtOH (1 mL) was added at – 78 °C and the reaction was stirred for 1.5 h while the temperature was allowed to rise to – 30 °C. The mixture was then cooled to – 78 °C. After addition of acetic acid (75 μL, 1.3 mmol, 2 equiv.), the temperature was slowly allowed to rise to 25 °C. After addition of 3 mL water, ethanol was removed under vacuum and the β-nitroseleno ether was extracted with diethyl ether (3 × 15 mL). The organic phase was dried ($MgSO_4$) and concentrated. Hydrogen peroxide (30%, 2 mL) was then added over 15 min to the β-nitroseleno ether in CH_2Cl_2 (2 mL) at 0° C and the mixture was stirred for 20 min at this temperature. After extraction with diethyl ether (3 × 20 mL), the organic phase was washed several times with aqueous sodium carbonate, dried over $MgSO_4$, and concentrated under reduced pressure. **(*Z*)-**nitroalkenes **1f** and **1g** were purified by flash chromatography on silica gel.

***(Z)*-(2-Nitroprop-2-en-1-yl)benzene (1f):** Yield 71%. – R_f = 0.73 (diethyl ether/petroleum ether = 70:30). – IR: $\tilde{\nu}$ = 2962, 1650, 1558, 1522, 1071 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.3 Hz, 3 H), 1.24–1.50 (m, 6 H), 2.16 (d, *J* = 1.3 Hz, 3 H), 2.43 (q, *J* = 7.1 Hz, 2 H), 5.81 (br. t, *J* = 7.1 Hz, 1 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.0, 19.2, 22.4, 28.6 (2 C), 31.5, 134.8, 146.5.

(*Z*)-2-Nitrooct-2-ene (1g): Yield 71%. – R_f = 0.73 (diethyl ether/petroleum ether = 70:30). – IR: $\tilde{\nu}$ = 2962, 1650, 1558, 1522, 1071 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 2.34 (d, *J* = 1.4 Hz, 3 H), 6.46 (br. s, 1 H), 7.24–7.33 (m, 5 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 20.1, 128.0, 128.7, 129.0, 132.1, 133.6, 146.4.

4-Chlorobut-2-yn-1-ol (2a):[31] Yield 73%. – R_f = 0.43 (diethyl ether/petroleum ether = 70:30. – IR: $\tilde{\nu}$ = 3351, 3024, 2230, 1430, 908, 697 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.84 (br. s, 1 H, OH), 4.16 (t, *J* = 2.0 Hz, 2 H), 4.30 (t, *J* = 2.0 Hz, 2 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 30.4, 51.1, 80.5, 84.7.

4-Methylsulfonylbut-2-yn-1-ol (2b): Methanesulfonyl chloride (100μL, 1.28 mmol, 1.28 equiv.) was added to a mixture of butynediol (1 mmol) and triethylamine (250μL, 1.79 mmol) at –50 °C; the temperature was allowed to rise to 0 °C. Ice water (5 mL) was added with stirring. The aqueous layer was extracted twice with dichloromethane (2 × 10 mL). The combined organic solutions were dried over $MgSO_4$ and subsequently concentrated in vacuo to afford crude **2b**: Yield 49.2 mg (30%). – R_f = 0.60 (diethyl ether). – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.11 (s, 3 H), 4.17 (t, *J* = 2.0 Hz, 2 H), 4.88 (t, *J* = 2.0 Hz, 2 H).

4-Tosyloxybut-2-yn-1-ol (2c): Sodium hydride (60% dispersion in mineral oil, 100 mg) was washed three times with petroleum ether; the solvent was removed in vacuo and THF (5 mL) was introduced under argon. To this suspension was added DMPU (1 mL) and butyne-1,4-diol (215 mg, 1 equiv.). Tosyl chloride (4.77 mg, 1 equiv.) in THF (5 mL) was slowly added; after stirring for 5 h at room temperature, the mixture was filtered on silica gel and extracted with diethyl ether (3 × 15 mL). The organic extracts were washed with water and dried on $MgSO_4$; crude monotosylate **2c** was recovered after filtration and concentration in vacuo. Yield 315 mg (52%). – R_f = 0.45 (diethyl ether). – IR: $\tilde{\nu}$ = 3389, 2924, 2210, 1597, 1446, 1175, 1095, 1019 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 3.98 (t, *J* = 2.0 Hz, 2 H), 4.73 (t, *J* = 2.0 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 7.80 (d, *J* = 8.1 Hz, 2 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 21.5, 50.3, 58.0, 81.0, 88.0, 128.0, 129.8, 132.7, 145.3.

4-(Tetrahydropyran-2-yloxy)but-2-yn-1-ol (2d):[60] Camphorsulfonic acid (232 mg, 1 mmol, 0.02 equiv.) was added in two fractions at –20 °C to a solution of prop-2-yn-1-ol (50 mmol) and 3,4-dihydro-2*H*-pyran (60 mmol, 5.4 mL, 1.2 equiv.) in 20 mL CH_2Cl_2. The reaction mixture was stirred for 12 h at room temperature, and the reaction was quenched with 10% aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (3 × 15 mL). The organic phase was washed with water and brine and dried over $MgSO_4$; after filtration and concentration under reduced pressure, 1-(tetrahydropyranyloxy)-2-propyne[61] (80%) was purified by flash chromatography on silica gel.

*n*BuLi in hexane (1.5 M, 3 mmol, 2 mL, 1.5 equiv.) was added dropwise under argon to the 1-(tetrahydropyranyloxy)-2-propyne (2.5 mmol) in THF (10 mL) at – 40 °C. After 15 min stirring at 0 °C, the reaction mixture was cooled to –10 °C and dry powdered paraformaldehyde (508 mg, 17.5 mmol, 7 equiv.) was added in small fractions. The mixture was vigorously stirred for 3 h in refluxing THF. After cooling at room temperature and addition of ice water (10 mL), the product was extracted with ether (3 × 20 mL), dried over $MgSO_4$, then concentrated under reduced pressure and purified by flash chromatography. **(2d)**: Yield 4.5 g (53%). – R_f = 0.21 (diethyl ether/petroleum ether = 70:30;). – IR: $\tilde{\nu}$ = 3424, 2942, 2867, 2018, 1116, 1021 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56–1.78 (m, 6 H), 3.54 (m, 1 H), 3.81 (m, 1 H), 4.30 (m, 4 H), 4.78 (t, *J* = 3.0 Hz, 1 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 18.8, 25.1, 30.0, 50.5, 54.2, 61.8, 80.9, 84.6, 96.6.

General Procedure for the Preparation of Nitroallenes (3a–c, e–g): *t*BuOK (67.3 mg, 0.6 mmol, 1.5 equiv.) in *t*BuOH (1 mL) was added at 0 °C under argon to a solution of nitroalkenes **1a**, **1b**, or **1d–f** (0.4 mmol) and 4-chlorobut-2-yn-1-ol **2** (0.6 mmol, 1.5 equiv.) in THF (2 mL) over a period of 15 min. The mixture was stirred at 0 °C for 10 min and then for a further 30–60 min at room temperature. After addition of water (5 mL) and extraction with diethyl ether (3 × 15 mL), the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Chromatography on silica gel afforded nitroallenes **3a–c** and **3e–g**.

3a-Nitro-3-vinylidene-hexahydrocyclopenta[*b*]furan (3a): Yield 63 mg (87%). – R_f = 0.56 (diethyl ether/ petroleum ether = 70:30). – IR: $\tilde{\nu}$ = 3066, 2970, 2855, 1987, 1965, 1541, 1360, 1058, 1027 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.85 (m, 4 H), 2.23 (m, 1 H), 2.47 (td, *J* = 12.0 and 4.5 Hz), 4.52 (dt, *J* = 11.1 and 2.8 Hz, 1 H), 4.56 (dt, *J* = 11.1 and 4.5 Hz, 1 H), 4.88 (br. d, *J* = 4.5 Hz, 1 H), 5.14 (ddd, *J* = 12.0, 4.5 and 3.0 Hz, 1 H), 5.19 (ddd, *J* = 12.0, 4.3 and 2.8 Hz, 1 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 24.2, 33.1, 36.7, 70.8, 82.7, 90.5, 102.2, 104.6, 200.8. – $C_9H_{11}NO_3$ (181.19): calcd. C 59.66, H 6.12, N 7.73; found C 59.55, H 6.20, N 7.68.

3a-Nitro-3-vinylidene-octahydrobenzofuran (3b): Yield 61 mg (78%). – R_f = 0.58 (diethyl ether/ petroleum ether = 70:30). – IR: $\tilde{\nu}$ =

3060, 2950, 2870, 1985, 1965, 1550, 1365, 1080, 1040 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.60–2.00 (m, 6 H), 2.20–2.35 (m, 2 H,), 4.49 (dt, *J* = 12.0 and 4.2 Hz, 1 H,), 4.58 (dt, *J* = 12.0 and 4.8 Hz, 1 H,), 4.67 (dd, *J* = 9.0 and 6.0 Hz, 1 H), 5.18 (ddd, *J* = 12.0, 4.8 and 4.2 Hz, 1 H), 5.22 (ddd, *J* = 12.0, 4.8 and 4.2 Hz, 1 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 21.6, 22.1, 27.7, 30.7, 66.2, 81.2, 82.8, 97.5, 100.6, 201.6. – MS: *m*/*z* (%) = 196 [M + 1]$^+$ (1), 149 (6), 99 (12), 87 (30), 81 (100), 69 (24). – $C_{10}H_{13}NO_3$ (195.22): calcd. C 61.53, H 6.71, N 7.17; found C 61.47, H 6.79, N 7.10.

Spiro Compound 3c: Yield 79 mg (78%). – R_f = 0.55 (ethyl acetate/benzene = 1:9) – IR: ṽ = 2960, 2910, 1985, 1960, 1540, 1080, 1050 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.50–1.60 (m, 2 H, H9), 1.70–1.80 (m, 2 H, H8), 2.20–2.30 (m, 2 H, H10), 4.10–3.85 (m, 4 H, H11), 4.54 (dt, *J* = 11.2 and 4.9 Hz, H4a), 4.62 (dt, *J* = 11.2 and 4.0 Hz, 1 H, H4b), 4.66 (s, 1 H, H1), 5.20 (ddd, *J* = 12.0, 4.9 and 4.0 Hz, H6a), 5.24 (ddd, *J* = 12.0, 4.9 and 4.0 Hz, H6b). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 19.13 (C9), 29.86 (C8), 32.85 (C10), 65.25 (C11a), 66.35 (C11b), 68.84 (C4), 83.24 (C6), 85.56 (C1), 98.18 (C3), 101.62 (C2), 108.75 (C7), 200.91 (C5). – $C_{12}H_{15}NO_5$ (253.26): calcd. C 56.91, H 5.97, N 5.53; found C 56.85, H 6.02, N 5.60.

2,3-Dimethyl-3-nitro-4-vinylidenetetrahydrofuran (3e): Yield 46 mg (68%). – R_f = 0.51 (diethyl ether/ petroleum ether = 70:30). – IR: ṽ = 2975, 2926, 2866, 1985, 1966, 1544, 1385, 1092, 1036 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.24 (d, *J* = 6.5 Hz, 3 H), 1.62 (s, 3 H), 4.48 (dt, *J* = 11.8 and 3.8 Hz, 1 H), 4.57 (dt, *J* = 11.8 and 4.6 Hz, 1 H), 4.63 (q, *J* = 6.5 Hz, 1 H), 5. 17 (t, *J* = 4.2 Hz, 2 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 15.6, 19.0, 67.4, 82.1, 83.0, 96.4, 103.9, 201.2. – $C_8H_{11}NO_3$ (169.18): calcd. C 56.80, H 6.55, N 8.28; found C 56.73, H 6.61, N 8.20.

3-Methyl-3-nitro-2-pentyl-4-vinylidenetetrahydrofuran (3f): Yield 65 mg (72%). – R_f = 0.69 (diethyl ether/ petroleum ether = 70:30). – IR: ṽ = 2957, 2860, 1984, 1967, 1547, 1383, 1341, 1080, 1037 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.9 Hz, 3 H, H12), 1.29 (m, 6 H, H9,10,11), 1.48 (m, 2 H, H8), 1.62 (s, 3 H, H7), 4.44 (t, *J* = 6.0 Hz, 1 H, H1), 4.45 (dt, *J* = 11.8 and 3.7 Hz, 1 H, H4α), 4.55 (dt, *J* = 11.8 and 4.9 Hz, 1 H, H4β), 5.15 (dd, *J* = 4.8 and 3.7 Hz, 2 H, H6). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.0, 18.9 (C7), 22.6 (C11), 25.4 (C9), 29.7 (C10), 31.7 (C8), 67.3 (C4), 83.0 (C6), 86.1 (C1), 96.3 (C3), 104.6 (C2), 200.8 (C5). – $C_{12}H_{19}NO_3$ (225.29): calcd. C 63.98, H 8.50, N 6.22; found C 63.91, N 6.27, H 8.48.

3-Methyl-3-nitro-2-phenyl-4-vinylidenetetrahydrofuran (3g): Yield 69 mg (75%). – R_f = 0.66 (diethyl ether/petroleum ether = 70:30). – IR: ṽ = 2984, 2930, 2859, 1985, 1965, 1543, 1520, 1496, 1453, 1324, 1058. –^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 3 H), 4.79 (t, *J* = 4.1 Hz, 2 H), 5.18 (t, *J* = 4.1 Hz, 2 H), 5.59 (s, 1 H), 7.25 (m, 3 H), 7.35 (m, 2 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 20.5, 68.8, 83.3, 88.0, 96.4, 104.8, 126.4, 128.6, 128.7, 136.2, 200.5. – $C_{13}H_{13}NO_3$ (231.25): calcd. C 67.52, H 5.67, N 6.06; found C 67.49, H 5.69, N 6.12.

Spiro Compound 3d: NaH (60% in oil, 26 mg, 0.64 mmol, 1.6 equiv.) was placed under argon in a 25 mL flask. The suspension was washed three times with petroleum ether (3 × 5 mL) and traces of solvent were evaporated in vacuo. After addition of THF (4 mL) and chlorobutynol **2a** (67 mg, 0.64 mmol, 1.5 equiv.), the solution was stirred between 0 °C and 10 °C for 50 min. Nitroalkene **1c** (74 mg, 0.4 mmol) in THF (2 mL) was added at –10 °C and the mixture was stirred between 0 °C and 5 °C for 30 min, then at 25 °C for 30 min. After removal of the solvent in vacuo, the crude product was diluted with saturated NH_4Cl and extracted with diethyl ether (3 × 15 mL). The combined organic extracts were washed with water, dried over $MgSO_4$, and concentrated in vacuo. Chromatography on silica gel afforded **3d** (71 mg, 70% yield), contaminated with traces of residual chlorobutynol **2a**. Further chromatography on silica gel (eluent: ethyl acetate/benzene = 1:9) afforded pure **3d**. Yield 49 mg (48%). – R_f = 0.38 (diethyl ether/petroleum ether = 70:30). – IR: ṽ = 2957, 2912, 2848, 1984, 1957, 1540, 1089, 1023 cm^{-1}. – ^1H NMR (200 MHz, $CDCl_3$): δ = 2.01–2.60 (m, 6 H, H7,9,10), 3.94–3.98 (m, 4 H, H11), 4.48 (dt, *J* = 12.0 and 4.5 Hz, 1 H, H4a), 4.59 (dt, *J* = 12.0 and 4.2 Hz, 1 H, H4b), 4.89 (dd, *J* = 9.5 and 6.5 Hz, 1 H, H1), 5.24 (t, *J* = 4.2 Hz, 1 H, H6). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 27.1 (C10), 30.7 (C9), 36.1 (C7), 64.7 (C11), 66.2 (C4), 81.1 (C1), 83.2 (C6), 96.6 (C3), 99.8 (C2), 107.3 (C8), 201.9 (C5). – $C_{12}H_{15}NO_5$ (253,26): calcd. C 56.91, H 5.97, N 5.53; found C 56.85, H 6.03, N 5.53.

2-(But-3-yn-1-yloxy)tetrahydropyran (4b):[62] Compound **4b** was obtained in 91% yield, following the preparation as for **2d**. – R_f = 0.69 (diethyl ether/petroleum ether = 70:30). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.52–1.90 (m, 6 H), 1.95 (t, *J* = 2.6 Hz, 1 H), 2.48 (td, *J* = 7.2 and 2.6 Hz, 2 H), 3.52 (m, 2 H), 3.81 (m, 2 H), 4.63 (t, *J* = 3.2 Hz, 1 H).

5-(Tetrahydropyran-2-yloxy)pent-2-yn-1-ol (4c):[63] 53% yield. – R_f = 0.20 (diethyl ether/ petroleum ether = 70:30). – IR: ṽ = 3414, 2940, 2863, 2264, 1080, 1034 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.47–1.89 (m, 7 H), 2.50 (tt, *J* = 7.0 and 2.3 Hz, 2 H), 3.46 (m, 2 H), 3.84 (m, 2 H), 4.21 (dt, *J* = 5.9 and 2.0 Hz, 1 H), 4.59 (t, *J* = 3.5 Hz, 1 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 19.3, 20.1, 25.2, 30.4, 50.7, 62.2, 65.6, 79.6, 82.5, 98.7.

Preparation of 1-Methanesulfonyl-5-(tetrahydropyran-2-yloxy)pent-2-yne (4d) and 2-(5-Chloropent-3-ynyloxy)tetrahydropyran (4e): Using a preparation analogous to that of **2b**, **4c** gave a mixture of **4d** and **4e** (3:1) in 86% yield.

Compound 4d: R_f = 0.37 (diethyl ether/petroleum ether = 70:30). – IR: ṽ = 3408, 2923, 2225, 1156, 1095, 1022, 800 cm^{-1}. –^1H NMR (400 MHz, $CDCl_3$): δ = 1.53–1.82 (m, 6 H), 2.50 (tt, *J* = 7.0 and 2.1 Hz, 2 H), 3.10 (s, 3 H), 3.52 (m, 2 H), 3.82 (m, 2 H), 4.59 (t, *J* = 3.5 Hz, 1 H), 4.83 (t, *J* = 2.1 Hz, 2 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 19.3, 20.1, 25.2, 30.3, 38.8, 58.3, 62.2, 64.9, 73.1, 87.9, 98.7.

Compound 4e: R_f = 0.68 (diethyl ether/petroleum ether = 70:30). – IR: ṽ = 2924, 2871, 2233, 1657, 1117, 1074, 1034, 803 cm^{-1}. –^1H NMR (400 MHz, $CDCl_3$): δ = 1.50–1.83 (m, 6 H), 2.53 (tt, *J* = 7.0 and 2.3 Hz, 2 H), 3.49 (m, 2 H), 3.82 (m, 2 H), 4.12 (t, *J* = 2.3 Hz, 2 H), 4.62 (t, *J* = 3.3 Hz, 1 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 19.3, 20.3, 25.4, 30.5, 31.0, 62.2, 65.3, 75.9, 84.4, 98.7.

2-(5-Bromopent-3-ynyloxy)tetrahydropyran (4f):[64] Anhydrous lithium bromide (35 mg, 0.4 mmol, 2 equiv.) was added to a solution of **4d** (0.2 mmol) in acetone (3 mL). After the mixture had been refluxed for 1 h, 10 mL of ice water was added to the suspension and the mixture was extracted with petroleum ether (3 × 15 mL); the combined extracts were washed with water and subsequently dried over $MgSO_4$. After removal of the solvent under reduced pressure, crude **4f** was utilized without further purification: 73% yield. – R_f = 0.66 (diethyl ether/petroleum ether = 70:30. – IR: ṽ = 2958, 2862, 2232, 1117, 1075, 1034, 807 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.59–1.79 (m, 6 H), 2.53 (tt, *J* = 7.0 and 2.3 Hz, 2 H), 3.51 (m, 2 H), 3.77 (m, 2 H), 3.90 (t, *J* = 2.3 Hz, 2

H), 4.62 (t, J = 3.3 Hz, 1 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 15.4, 19.4, 20.6, 25.5, 30.6, 62.3, 65.4, 76.2, 85.0, 98.8.

Preparation of Halo Alcohols 4g and 4h: A camphorsulfonic acid solution (3% 14 mL) in THF/H_2O = 30 (14 mL) was added dropwise to 1 mmol of **4e** or **4f** in 10 mL THF. The mixture was stirred for 3 days at room temperature and extracted with diethyl ether (3 × 15 mL); the combined extracts were washed with saturated $NaHCO_3$, with water and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the alcohols were purified by flash chromatography on silica gel.

5-Chloropent-3-yn-1-ol (4g): 73% yield. – R_f = 0.24 (diethyl ether/petroleum ether = 1:1. – IR: ṽ = 3359, 2918, 2843, 2233, 1098, 1043, 798 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.28 (br. s, 1 H, OH), 2.47 (tt, J = 6.2 and 2.2 Hz, 2 H), 3.69 (br. t, J = 6.2 Hz, 2 H), 4.11 (t, J = 2.2 Hz, 2 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 23.1, 30.9, 60.7, 76.8, 84.1.

5-Bromopent-3-yn-1-ol (4h): 93% yield. – R_f = 0.21 (diethyl ether/petroleum ether = 1:1). – IR: ṽ = 3355, 2921, 2227, 1091, 1040, 799 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.76 (t, J = 6.0 Hz, 1 H, OH), 2.50 (tt, J = 6.2 and 2.3 Hz, 2 H), 3.71 (q, J = 6.2 Hz, 2 H), 3.90 (t, J = 2.3 Hz, 2 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 15.2, 23.0, 60.5, 76.8, 84.6.

General Procedure for the Preparation of Nitroallenes 5a, 5b, 5e, 5f, and 5g: *t*BuOK (67.3 mg, 0.6 mmol, 1.5 equiv.) in *t*BuOH (1 mL) was added at 0 °C under argon over a period of 15 min to a solution of nitroalkenes **1a**, **1b**, or **1d**–**f** (0.4 mmol) in THF (2 mL), containing 5-chloropent-3-yn-1-ol **4g**, or 5-bromopent-3-yn-1-ol **4h** (0.6 mmol, 1.5 equiv.). The mixture was stirred at 0 °C for 10 min and a further 30–60 min at room temperature. After addition of water (5 mL) and extraction with diethyl ether (3 × 15 mL), the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. Chromatography on silica gel afforded the nitroallenes.

4a-Nitro-4-vinylideneoctahydrocyclopenta[*b*]pyran (5a): Yield 53 mg (68%). – R_f = 0.59 (diethyl ether/petroleum ether = 1:1). – IR: ṽ = 2962, 2848, 1954, 1542, 1359, 1094, 1022 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.63–1.95 (m, 4 H), 2.26 (m, 1 H), 2.36–2.48 (m, 2 H), 2.55 (m, 1 H), 3.64 (ddd, J = 11.3, 8.3 and 5.3 Hz, 1 H, H5a), 3.96 (ddd, J = 11.3, 5.3 and 4.5 Hz, 1 H, H5b), 4.55 (dd, J = 4.5 and 1.2 Hz, H1), 4.89 (dt, J = 11.2 and 2.8 Hz, 1 H, H7a), 4.95 (dt, J = 11.2 and 2.8 Hz, 1 H, H7b). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 20.8, 27.3 (C4), 29.3, 33.0, 65.0 (C5), 79.3 (C7), 83.4 (C1), 96.9 (C3 or C2), 97.0 (C2 or C3), 203.8 (C6). – $C_{10}H_{13}NO_3$ (195.22): calcd. C 61.53, H 6.71, N 7.17; found C 61.48, H 6.75, N 7.08.

4a-Nitro-4-vinylideneoctahydrochromene (5b): Yield 62 mg (74%). – R_f = 0.61 (diethyl ether/ petroleum ether = 1:1). – IR: ṽ = 2982, 2859, 1960, 1546, 1342, 1094, 1016 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36–2.26 (m, 8 H), 2.32–2.42 (m, 2 H, H4), 3.64 (dt, J = 11.5 and 5.7 Hz, 1 H, H5a), 3.95 (dt, J = 11.5 and 5.7 Hz, 1 H, H5b), 4.45 (dd, J = 7.6 and 3.1 Hz, 1 H, H1), 4.91 (dt, J = 11.2 and 2.6 Hz, 1 H, H7a), 4.96 (dt, J = 11.2 and 2.6 Hz, 1 H, H7b). –^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.4 (2C), 27.0, 28.3 (C4), 31.8, 63.7 (C5), 75.7 (C1), 79.1 (C7), 91.7 (C3), 97.9 (C2), 204.2 (C6). – $C_{11}H_{15}NO_3$ (209.25): calcd. C 63.14, H 7.23, N 6.69; found C 63.08, H 7.25, N 6.63.

2,3-Dimethyl-3-nitro-4-vinylidenetetrahydropyran (5e): Yield 50 mg (68%). –R_f = 0.60 (diethyl ether/ petroleum ether = 1:1). – IR: ṽ = 2962, 2848, 1958, 1544, 1345, 1093, 1017. cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, J = 6.6 Hz, 3 H), 1.58 (s, 3 H, H8), 2.34 (dddt, J = 16.7, 7.1, 4.6 and 2.4 Hz, 1 H, H4a), 2.43 (dddt, J = 16.7, 6.8, 4.7 and 2.4 Hz, 1 H, H4b), 3.66 (ddd, J = 11.4, 7.0 and 4.5 Hz, 1 H, H5a), 3.91 (ddd, J = 11.4, 6.6 and 4.7 Hz, 1 H, H5b), 4.54 (q, J = 6.6 Hz, 1 H, H1), 4.90 (dt, J = 11.1 and 2.6 Hz, 1 H, H7a), 4.96 (dt, J = 11.1 and 2.6 Hz, 1 H, H7b). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.9, 19.4 (C8), 28.3 (C4), 64.1 (C5), 75.9 (C1), 79.4 (C7), 91.7 (C3), 99.4 (C2), 203.6 (C6). – MS: m/z (%) = 137 (13), 111 (24), 91 (12), 79 (10), 67 (33), 65 (18), 55 (11), 53 (20), 43 (100), 41 (28). – $C_9H_{13}NO_3$ (183.21): calcd. C 59.00, H 7.15, N 7.65; found C 58.94, H 7.19, N 7.60.

3-Methyl-3-nitro-2-pentyl-4-vinylidenetetrahydropyran (5f): Yield 79 mg (83%). – R_f = 0.62 (diethyl ether/petroleum ether = 1:1). – IR: ṽ = 2981, 2859, 1962, 1545, 1349, 1098, 1021. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, J = 6.8, 3 H), 1.22–1.35 (m, 6 H), 1.49 (m, 2 H), 1.58 (s, 3 H, H8), 2.33–2.43 (m, 2 H, H4), 3.62 (ddd, J = 11.2, 7.6 and 4.6 Hz, 1 H, H5a), 3.88 (dt, J = 11.2 and 5.5 Hz, 1 H, H5b), 4.27 (dd, J = 10.4 and 2.4 Hz, 1 H, H1),4.88 (dt, J = 11.0 and 2.6 Hz, 1 H, H7a), 4.94 (dt, J = 11.0 and 2.6 Hz, 1 H, H7b). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.1, 19.2 (C8), 22.6, 25.3, 28.2 (2C, C4 and $-CH_2-CH_3$), 31.6, 64.4 (C5), 79.3 (C1), 79.9 (C7), 91.6 (C3), 100.0 (C2), 202.9 (C6). – $C_{13}H_{21}NO_3$ (239.32): calcd. C 65.25, H 8.84, N 5.85; found C 65.20, H 8.88, N 5.89.

3-Methyl-3-nitro-2-phenyl-4-vinylidenetetrahydropyran (5g): Yield 74 mg (75%). – R_f = 0.63 (diethyl ether/petroleum ether = 1:1). – IR: ṽ = 3044, 2964, 1958, 1596, 1551, 1533 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 3 H, H8), 2.54 (m, 2 H, H4), 3.82 (td, J = 11.3 and 3.6 Hz, 1 H, H5a), 4.22 (ddd, J = 11.3, 5.5 and 2.5 Hz, 1 H, H5b), 4.87 (ddd, J = 11.0, 4.4 and 0.9 Hz, 1 H, H7a), 5.00 (ddd, J = 11.0, 4.1 and 0.9 Hz, 1 H, H7b), 5.33 (s, 1 H, H1), 7.21–7.35 (m, 5 H). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 18.0 (C8), 28.1 (C4), 67.7 (C5), 79.9 (C7), 82.6 (C1), 92.1 (C3), 101.3 (C2), 127.6, 128.4, 135.6, 201.3 (C6). – $C_{14}H_{15}NO_3$ (245.28): calcd. C 68.56, H 6.16, N 5.71; found C 68.51, H 6.20, N 5.65.

3-Methyl-2-pentyl-4-vinylidenetetrahydrofuran-3-amine (6f): Diiodomethane (0.333 g, 1.24 mmol) was added dropwise to a suspension of samarium metal (0.230 g, 1.53 mmol) in dry THF (12 mL) under argon. A deep blue color rapidly developed and the resulting solution was stirred at ambient temperature for 1 h. A solution of nitroallene **3f** (0.2 mmol) containing *t*BuOH (38 mL, 0.4 mmol, 2 equiv.) in THF (2 mL) was added to the freshly prepared 0.1 M SmI_2-THF solution and the resulting mixture was stirred at room temperature for 30 min.

After filtration through Celite and extraction with diethyl ether (4 × 15 mL), the combined extracts were washed with brine and dried over $MgSO_4$. After concentration in vacuo, the crude product did not require further purification to give correct spectroscopic data. – **Compound 6f:** Yield 16 mg (42%). – R_f = 0.29 (ethyl acetate/petroleum ether = 1:2). – IR: ṽ = 3367, 2964, 1965, 1092, 1021 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.0 Hz, 3 H), 1.14 (s, 3 H, H7), 1.19–1.81 (m, 8 H), 3.90 (t, J = 1.8 Hz, 1 H, H1), 4.35 (dt, J = 12.3 and 4.7 Hz, 1 H, H4a), 4.46 (dt, J = 12.3 and 4.2 Hz, 1 H, H4b), 4.46 (dt, J = 9.8 and 4.5 Hz, 1 H, H6a), 4.80 (dt, J = 9.8 and 4.5 Hz, 1 H, H6b). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.2, 22.6 (C7), 22.7, 26.7, 29.2, 32.1, 66.6 (C4), 71.1 (C2), 81.3 (C6), 88.1 (C1), 103.9 (C3), 197.6 (C5). – MS: m/z (%) = 196 $[M + 1]^+$ (26), 194 (23), 178 (30), 123 (48), 99 (47), 95 (56), 82 (100).

Allenylhydroxylamines 7a, 7b, 7g, 7e, and 8b: A solution of nitroallene (0.2 mmol) containing *t*BuOH (38 μL, 0.4 mmol) in THF

(2 mL) was added to a freshly prepared 0.1 M SmI_2-THF solution (0.8 mmol, 4 equiv.) at 0 °C under argon. The reaction mixture was stirred for 10 min at 0 °C, and after filtration through Celite, addition of water (5 mL), and extraction with diethyl ether (3 × 15 mL), the combined extracts were washed with brine and dried over $MgSO_4$. After concentration under reduced pressure, crude α-allenylhydroxylamines were isolated.

***N*-(3-Vinylidene-hexahydrocyclopenta[*b*]furan-3a-yl)hydroxylamine (7a):** Yield 20 mg (60%). – R_f = 0.20 (ethyl acetate/petroleum ether = 1:2). – IR: $\tilde{\nu}$ = 3350- 3241(broad), 2960, 2854, 1967, 1055, 1011 cm^{-1}. – ^1H NMR (400 MHz, C_6D_6): δ = 1.57–1.98 (m, 6 H, H7,8,9), 4.46 (dt, *J* = 11.3 and 3.4 Hz, 1 H, H4a), 4.52 (dt, *J* = 11.3 and 4.2 Hz, 1 H, H4b), 4.57 (br. d, *J* = 4.5 Hz, 1 H, H1), 4.76 (t, *J* = 3.8 Hz, 2 H, H6). – ^{13}C NMR (100.61 MHz, C_6D_6): δ = 24.2 (C8), 33.4 (C7), 35.6 (C9), 70.3 (C4), 79.6 (C2), 80.0 (C6), 87.5 (C1), 107.6 (C3), 199.2 (C5). – $C_9H_{13}NO_2$ (167.21): calcd. C 64.65, H 7.84, N 8.38; found C 64.60, H 7.89, N 8.28.

***N*-(3-Vinylidene-hexahydrobenzofuran-3a-yl)hydroxylamine (7b):** Yield 22 mg (60%). – R_f = 0.24 (ethyl acetate/petroleum ether = 1:2). – IR: $\tilde{\nu}$ = 3354–3264 (broad), 2922, 2846, 1967, 1026 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.51–2.02 (m, 8 H, H7,8,9,10), 4.12 (dd, *J* = 8.7 and 5.9 Hz, 1 H, H1), 4.45 (dt, *J* = 12.2 and 4.4 Hz, 1 H, H4a), 4.52 (dt, *J* = 12.2 and 4.4 Hz, 1 H, H4b), 4.95 (dt, *J* = 10.6 and 4.4 Hz, 1 H, H6a), 5.00 (dt, *J* = 10.6 and 4.4 Hz, 1 H, H6b). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.1 (2C, C8 and C9), 27.2 (C7), 28.7 (C10), 66.0 (C4), 69.8 (C2), 78.8 (C1), 81.0 (C6), 102.6 (C3), 199.5 (C5). – $C_{10}H_{15}NO_2$ (181.24): calcd. C 66.27, H 8.34, N 7.73; found C 66.21, H 8.40, N 7.70.

***N*-(2,3-Dimethyl-4-vinylidene-tetrahydrofuran-3-yl)hydroxylamine (7e):** Yield 20 mg (65%). – R_f = 0.22 (ethyl acetate/petroleum ether = 1:2). – IR: $\tilde{\nu}$ = 3596–3560, 3279, 3049, 1966 cm^{-1}. – ^1H NMR (400 MHz, C_6D_6): δ = 1.21 (d, *J* = 6.4 Hz, 3 H, H7), 1.23 (s, 3 H, H8), 4.24 (q, *J* = 6.4 Hz, 1 H, H1), 4.39 (t, *J* = 4.3 Hz, 2 H, H4), 4.76 (t, *J* = 4.3 Hz, 1 H, H6). – ^{13}C NMR (100.61 MHz, C_6D_6): δ = 15.8 (C7), 17.9 (C8), 67.0 (C4), 69.8 (C2), 80.2 (C1), 80.5 (C6), 106.4 (C3), 199.5 (C5). – $C_8H_{13}NO_2$ (155.20): calcd. C 61.91, H 8.44, N 9.03; found C 61.92, H 8.50, N 9.10.

***N*-(3-Methyl-2-phenyl-4-vinylidene-tetrahydrofuran-3-yl)hydroxylamine (7g):** Yield 26 mg (60%). – R_f = 0.23 (ethyl acetate/petroleum ether = 1:2). – IR: $\tilde{\nu}$ = 3555, 3257, 3033, 2969, 2928, 2859, 1966, 1058 cm^{-1}. – ^1H NMR (400 MHz, C_6D_6): δ = 0.79 (s, 3 H, H11), 4.52 (dt, *J* = 11.9 and 5.0 Hz, 1 H, H4a), 4.60 (dt, *J* = 11.9 and 3.5 Hz, 1 H, H4b), 4.70 (ddd, *J* = 10.3, 4.9 and 3.4 Hz, 1 H, H6a), 4.76 (ddd, *J* = 10.3, 5.2 and 3.6 Hz, 1 H, H6b), 5.20 (s, 1 H, H1), 7.12 (t, *J* = 7.4 Hz, 1 H, H10), 7.21 (t, *J* = 7.4 Hz, 2 H, H9), 7.50 (d, *J* = 7.4 Hz, 2 H, H8). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 20.4 (C11), 68.6 (C4), 71.4 (C2), 81.2 (C6), 84.3 (C1), 106.9 (C3), 127.2 (C8), 128.0 (C10), 128.7 (C9), 139.8 (C7), 199.2 (C5). – $C_{13}H_{15}NO_2$ (217.27): calcd. C 71.87, H 6.96, N 6.45; found C 71.79, H 7.02, N 6.39.

***N*-(4-Vinylidene-hexahydrochromen-4a-yl)hydroxylamine (8b):** Yield 25 mg (63%). – R_f = 0.28 (ethyl acetate/petroleum ether = 1:2). – IR: $\tilde{\nu}$ = 3590–3162 (broad), 2962, 2857, 1957, 1093, 1020, 797 cm^1. – ^1H NMR (400 MHz, C_6D_6): δ = 1.25–1.85 (m, 6 H, H8,9,10), 1.95–2.25 (m, 4 H, H4,11), 3.39 (dt, *J* = 11.2 and 6.0 Hz, 1 H, H5a), 3.71 (dt, *J* = 11.2 and 5.5 Hz, 1 H, H5b), 3.93 (t, *J* = 3.1 Hz, 1 H, H1), 4.65 (dt, *J* = 9.7 and 2.7 Hz, 1 H, H7a), 4.75 (dt, *J* = 9.7 and 2.7 Hz, 1 H, H7b). – ^{13}C NMR (100.61 MHz, C_6D_6): δ = 22.0 (2C, C9 and C10), 27.0 (C8), 28.9 (C4), 30.6 (C11), 60.7 (C5), 64.4 (C2), 75.2 (C1), 76.8 (C7), 80.9 (C3), 204.4 (C6). – $C_{11}H_{17}NO_2$ (195.26): calcd. C 67.66, H 8.78, N 7.17; found C 67.58, H 8.83, N 7.09.

Oxazines 9a, 9b, 9e, 9g and 10b: A solution of α-allenylhydroxylamines **7a**, **7b**, **7e**, **7g**, or **8b** (0.1 mmol) in 3 mL $CHCl_3$ was slowly cyclized to give isomeric oxazines **9a**, **9b**, **9e**, **9g**, or **10b** by allowing to stand for 6 h-15d at either −20 °C or room temperature (Table 3). After completion of isomerization, as verified by NMR, the solvent was removed under reduced pressure and crude products were purified by flash chromatography on silica gel.

1,2,3,3a,5,7-Hexahydro-4,8-dioxa-9-azacyclopenta[*c*]indene (9a): Yield 11 mg (65%). – R_f = 0.18 (ethyl acetate/petroleum ether = 1:2). – IR: $\tilde{\nu}$ = 3359, 2962, 2917, 2858, 1652, 1094, 1040, 802 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.53–2.14 (m, 6 H, H7,8,9), 4.03 (m, 1 H, H1), 4.20 (ddd, *J* = 16.2, 5.2 and 3.0 Hz, 1 H, H6a), 4.26 (ddd, *J* = 16.2, 4.9 and 2.1 Hz, 1 H, H6b), 4.38 (ddd, *J* = 12.1, 3.4 and 1.7 Hz, 1 H, H4a), 4.49 (ddd, *J* = 12.1, 5.2 and 3.1 Hz, 1 H, H4b), 5.57 (quint, *J* = 2.2 Hz, 1 H, H5). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 24.8 (C8), 33.6 (C7), 36.3 (C9), 65.8 (C6), 70.1 (C4), 72.1 (C2), 87.2 (C1), 113.8 (C5), 142.0 (C3). – MS: *m*/*z* (%) = 168 (11), 167 [M^+] (11), 85 (13), 83 (11), 71 (26). – $C_9H_{13}NO_2$ (167.21): calcd. C 64.65, H 7.84, N 8.38; found C 64.58, H 7.90, N 8.28.

3,8-Dioxa-2-azatricyclo[7.4.0.0.^{1,6}]tridec-5-ene (9b): Yield 17 mg (92%). – R_f = 0.19 (ethyl acetate/petroleum ether = 1:2). – IR: $\tilde{\nu}$ = 3338, 3266, 3219, 2930, 2853, 1657, 1011 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.33–1.61 (m, 6 H, H7,8,9), 1.95–2.07 (m, 2 H, H10), 3.44 (br. t, *J* = 2.8 Hz, 1 H, H1), 4.14 (dq, *J* = 16.0 and 3.0 Hz, 1 H, H6a), 4.21 (ddt, *J* = 16.0, 3.1 and 2.1 Hz, 1 H, H6b), 4.34 (dq, *J* = 12.6 and 2.5 Hz, 1 H, H4a), 4.53 (ddt, *J* = 12.6, 3.0 and 2.1 Hz, 1 H, H4b), 5.55 (tt, *J* = 3.5 and 2.0 Hz, 1 H, H5). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 20.0 (C8), 21.1 (C9), 27.1 (2 C, C7 and C10), 60.3 (C2), 66.2 (C6), 68.2 (C4), 79.1 (C1), 114.9 (C3), 142.9 (C5). – MS: *m*/*z* (%) = 182 (11), 181 [M^+] (100), 150 (18), 149 (25), 111 (10), 96 (5), 83 (7).

3,3a-Dimethyl-1,3a,4,6-tetrahydro-*3H*-2,5-dioxa-4-azaindene (9e): Yield 11 mg (72%). – R_f = 0.20 (ethyl acetate/petroleum ether = 1:2). – IR: $\tilde{\nu}$ = 3375, 2921, 2855, 1657, 1078, 1006 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.20 (d, *J* = 6.3 Hz, 3 H, H7), 1.27 (s, 3 H, H8), 3.50 (q, *J* = 6.3 Hz, 1 H, H1), 4.21 (m, 2 H, H6), 4.30 (ddd, *J* = 12.6, 4.2 and 2.2 Hz, 1 H, H4a), 4.48 (ddd, *J* = 12.6, 5.5 and 3.0 Hz, 1 H, H4b), 5.56 (quint, *J* = 2.2 Hz, 1 H, H5). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 14.9 (C7), 16.5 (C8), 61.8 (C2), 66.0 (C6), 68.1 (C4), 79.6 (C1), 114.9 (C5), 142.7 (C3). – MS: *m*/*z* (%) = 155 [M^+] (9), 14 (27), 111 (12), 71 (28), 55 (16), 43 (44), 28 (100).

3a-Methyl-3-phenyl-1,3a,4,6-tetrahydro-3*H*-2,5-dioxa-4-azaindene (9g): Yield 17 mg (80%). – R_f = 0.22 (ethyl acetate/petroleum ether = 1:2). – IR: $\tilde{\nu}$ = 3356, 2962, 2917, 2845, 2917, 2845, 1651, 1630, 1558, 1539, 1453, 1093, 1016 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00 (s, 3 H, H11), 4.21 (ddd, *J* = 16.0, 5.7 and 2.9 Hz, 1 H, H6a), 4.34 (ddd, *J* = 16.0, 4.3 and 2.0 Hz, 1 H, H6b), 4.52 (ddd, *J* = 12.5, 4.1 and 2.0 Hz, 1 H, H4a), 4.59 (s, 1 H, H1), 4.69 (ddd, *J* = 12.5, 5.5 and 3.1 Hz, 1 H, H4b), 5.67 (m, 1 H, H5), 7.25–7.35 (m, 5 H, H8,9,10). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 17.8 (C11), 63.4 (C2), 66.3 (C6), 68.4 (C4), 85.6 (C1), 116.1 (C5), 126.0 (C8), 128.0 (C10), 128.5 (C9), 137.7 (C7), 142.0 (C3) – MS: *m*/*z* (%) = 141(7), 111 (100), 110 (26), 105 (42), 94 (9), 77 (29), 43 (50).

3,9-Dioxa-2-azatricyclo[8.4.0.0.^{1,6}]tetradec-5-ene (10b): Yield 14 mg (71%). – R_f = 0.22 (ethyl acetate/petroleum ether = 1:2). – IR:

$\tilde{\nu}$ = 3341, 2961, 2854, 1652, 1630, 1103, 1041 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46–1.86 (m, 6 H, H8,9,10), 2.04–2.40 (m, 2 H, H11), 2.40–2.50 (m, 2 H, H4), 3.12 (br. s, 1 H, H1), 3.65 (m, 1 H, H5a), 3.96 (m, 1 H, H5b), 4.10 (dt, J = 15.9 and 3.4 Hz, 1 H, H7a), 4.33 (br. d, J = 15.9 Hz, 1 H, H7b), 5.50 (m, 1 H, H6). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 19.5 (C9 or C10), 20.6 (C10 or C9), 26.6 (C8), 27.9 (C4), 32.5 (C11), 57.7 (C2), 68.4 (C5 or C7), 69.1 (C7 or C5), 77.3 (C1), 118.6 (C6), 138.5 (C3) – $C_{11}H_{17}NO_2$ (195.26): calcd. C 67.66, H 8.78, N 7.17; found C 67.58, H 8.82, N 7.08.

Acetyldihydrofurans 11a and 11b: $AgBF_4$ (0.39 mmol, 0.5 equiv.) was added at room temperature under argon to a solution of allenylhydroxylamine **7a** or **7b** (0.78 mmol) in CH_2Cl_2. The mixture was stirred for 60 h and, after addition of brine (10 mL) and filtration on silica gel, the product was extracted with $CHCl_3$ (3 × 15 mL). The organic phase was washed and dried over $MgSO_4$. The solvent was removed under reduced pressure and crude products were purified by flash chromatography on silica gel.

1-(4,5,6,6a-Tetrahydro-2*H*-cyclopenta[*b*]furan-3-yl)ethanone (11a): Yield 12 mg (10%). – R_f = 0.46 (diethyl ether/petroleum ether = 70:30). – IR: $\tilde{\nu}$ = 2940, 2861, 1686, 1651, 1097, 1055 cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.50–2.06 (m, 4 H, H6,8), 2.27 (s, 3 H, H5), 2.56 (m, 1 H, H7ax), 3.49 (m, 1 H, H7eq), 5.12 (m, 2 H, H4), 5.18 (m, 1 H, H1). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 23.4 (C8), 26.0 (C6), 30.7 (C7), 31.1 (C5), 81.1 (C4), 93.9 (C1), 131.1 (C3), 162.4 (C2), 194.3 (C10).

1-(2,4,5,6,7,7a-Hexahydrobenzofuran-3-yl)ethanone (11b): Yield 21 mg (16%). – R_f = 0.48 (diethyl ether/petroleum ether = 70:30). – IR: $\tilde{\nu}$ = 3156, 2943, 2862, 1684, 1648, 1097 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23–1.44 (m, 4 H, H8,9), 1.83 (m, 2 H, H6), 1.93 (m, 1 H, H7ax), 2.26 (s, 3 H, H5), 3.35 (br. d, J = 14 Hz, 1 H, H7eq), 4.65 (m, 1 H, H1), 4.80 (dt, J = 11.6 and 3.5 Hz, 1 H, H4a), 4.86 (dd, J = 11.6, 5.2 and 1.8 Hz, 1 H, H4b). – ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 23.0 (C9), 26.5 (C8), 27.0 (C7), 30.6 (C5), 35.5 (C6), 75.4 (C4), 87.7 (C1), 129.3 (C3), 153.4 (C2), 195.3 (C10).

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