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Intermolecular Reactions of *N*-Alkoxycarbonyliminium Ions with Propargyltrimethylsilane; Oxazinone versus Allene Formation

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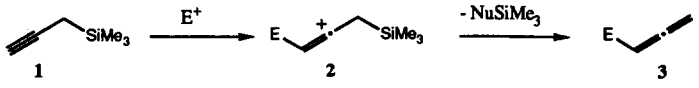
Key Words: propargylsilanes; N-acyliminium ions; 3,4-dihydro-2H-1,3-oxazin-2-ones; allenes; β-silyl cation.

Abstract: *Intermolecular reactions of N-alkoxycarbonyliminium ions with propargyltrimethylsilane mainly lead to 6-(trimethylsilyl)methyl-3,4-dihydro-2H-1,3-oxazinones, formed by intramolecular trapping of a stabilized β-silyl vinylic cation. α-Allenyl carbamates are obtained as minor products. The oxazinone/allene ratio is dependent on the nature of the Lewis acid and the solvent used.*

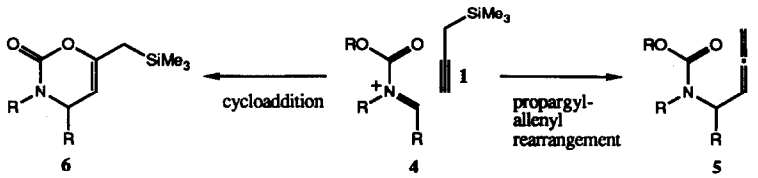
INTRODUCTION

The use of organosilicon reagents in organic synthesis has seen an enormous development in the last two decades.[1] Propargyltrimethylsilane (**1**) is such a reagent, which has proved useful for the preparation of mono-substituted allenes (**3**, eq 1). Silane **1** reacts with various electrophilic species E^+ such as acid chlorides,[2] acetals,[3] aldehydes,[4,5] ketones,[5,6] Michael acceptors,[6] and *N*-acyliminium[7] and oxonium[8] ions. These reactions are characterized by a propargyl-allenyl rearrangement, which proceeds through the intermediacy of a vinylic carbocation **2**, stabilized by a β-silicon atom.[9]



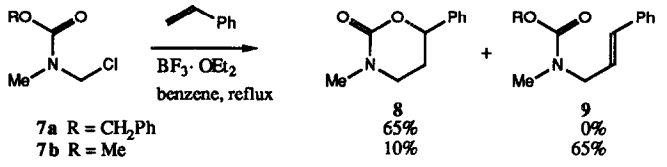
1 **2** **3** (eq 1)

In conjunction with our work on the application of electrophilic iminium species in synthesis[10] we anticipated that reaction of **1** with *N*-alkoxycarbonyliminium ion **4** (eq 2) might be a useful route to protected α-allenic amines **5**.[11-14] Such amines are interesting synthetic targets because of their biological activity as inhibitors of monoamine oxidases,[12] vitamin B_6 linked decarboxylases[13] and pyridoxal-phosphate dependent enzymes.[14]



6 **4** **5** (eq 2)

N-Alkoxycarbonyliminium ion **4**, however, can also be regarded as a hetero-1,3-diene which can react with propargyltrimethylsilane **1** via a $[\pi 4_s + \pi 2_s]$-cycloaddition[15] to furnish 3,4-dihydro-2*H*-1,3-oxazin-2-one **6**. Hetero Diels-Alder reactions of iminium ions **4** with alkenes are known in the literature.[16] The *N*-benzyloxycarbonyliminium ion derived from **7a** (eq 3), for example, reacts with styrene to give oxazinone **8**.[16a] The formation of both the cycloaddition product **8** and the addition product **9**, when methyl carbamate **7b** is used, indicates that this hetero Diels-Alder proceeds by a stepwise mechanism. In this paper,[17] we detail the results of the intermolecular reaction of **1** with iminium ion **4** and discuss the relevance of β-silyl cation **2** in this process. Recently, intramolecular reactions of *N*-alkoxycarbonyliminium ions with propargylsilanes have been reported.[18]

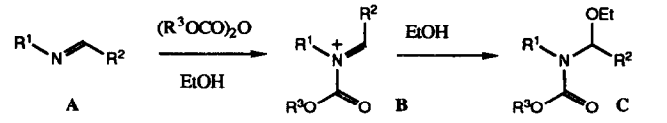


(eq 3)

7a R = CH_2Ph **8** 65% **9** 0%
7b R = Me 10% 65%

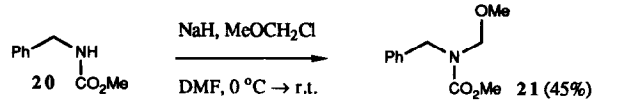
PREPARATION OF α-ALKOXYCARBAMATES 14-19, 21 AND 22

Because of their good stability, imines **10-13**[19] (Table 1) were selected for the synthesis of the *N*-alkoxycarbonyliminium ion precursors **C** (eq 4) by a method developed in our group.[20] Reaction of imine **A** with a dialkyl pyrocarbonate in ethanol proceeds through the intermediacy of iminium ion **B**, which is trapped by the solvent to give α-ethoxycarbamates **C**. The reaction rate strongly depended upon the electron-donating or -withdrawing property of the imine R^2 substituent. Conversion of the *p*-methoxyphenyl imine **10** (entry 1) to carbamate **14** proceeded at 60-70 °C in 17 h, while the electron-withdrawing *p*-nitro group in imine **12** (entry 3) retarded the reaction, so that even after 48 h (with 2.2 equiv of pyrocarbonate), the reaction was incomplete. The heterocyclic imine **13** (entry 6) reacted very smoothly at room temperature (because of the high nucleophilicity of the imine nitrogen) to give precursor **19** in excellent yield. This precursor, however, was less stable then its phenyl analogues and could be stored in the refrigerator for only a limited period of time. To study the influence of the nature of the *N*-substituent, the *tert*-butyl and benzyl carbamates **17** and **18** (entries 4 and 5) were synthesized. Due to some difficulties to remove the byproducts $PhCH_2OH$ and $EtOCOOCH_2Ph$, precursor **18** was obtained in a moderate yield (55%).

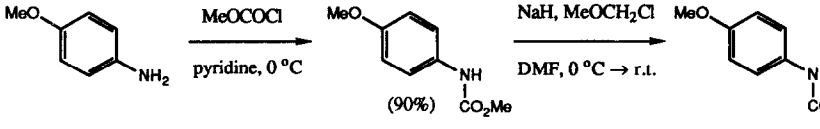


(eq 4)

The methodology illustrated in eq 4 could not be applied to imines with R^2 = alkyl or H because of their instability. Therefore, α-methoxycarbamate **21** (eq 5) was prepared by alkylation of carbamate **20**[21] with chloromethyl methyl ether. In order to study the influence of an aryl substituent at the nitrogen atom on the course of the reaction with propargyltrimethylsilane, precursor **22** (eq 6) was synthesized from *p*-anisidine.

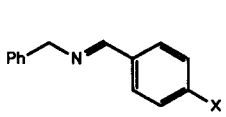
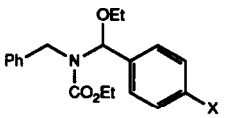
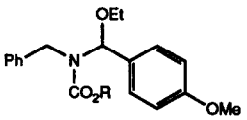
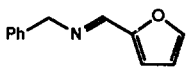
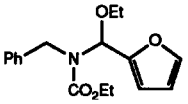


(eq 5)



(eq 6)

Table 1. Synthesis of the *N*-Alkoxycarbonyliminium Ion Precursors

entry	imine	pyrocarbonate (equiv)	conditions	time	product (yield)
					
1	**10** X = OMe	$(EtOCO)_2O$ (1.2)	60-70 °C	17 h	**14** X = OMe (84%)
2	**11** X = H	$(EtOCO)_2O$ (1.2)	60-70 °C	24 h	**15** X = H (82%)
3	**12** X = NO_2	$(EtOCO)_2O$ (2.2)[a]	60-70 °C	48 h	**16** X = NO_2 (51%)
					
4	**10**	$(t\text{-}BuOCO)_2O$ (2.0)	60-70 °C	24 h	**17** R = *t*-Bu (80%)
5	**10**	$(PhCH_2OCO)_2O$ (1.3)	60-70 °C	24 h	**18** R = $PhCH_2$ (55%)
					
6	**13**	$(EtOCO)_2O$ (1.2)	r.t.	1 h	**19** (96%)

[a] Initially 1.2 equiv, after 24 h another 1.0 equiv was added.

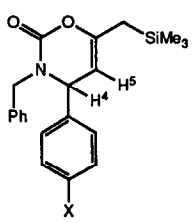
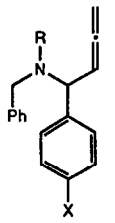
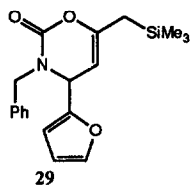
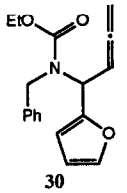
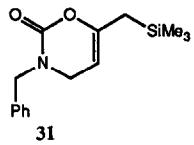
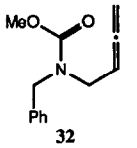
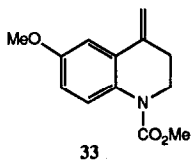
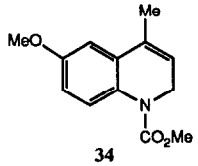
REACTIONS OF 14-19, 21 AND 22 WITH PROPARGYLTRIMETHYLSILANE

The precursors **14-19** and **21-22** (Table 2) were treated with propargyltrimethysilane **1** (3 equiv) under several conditions. Reaction of carbamate **14** (entry 1) in dichloromethane induced by tin tetrachloride (1.2 equiv, 0 °C → r.t.) gave after work-up (aq $NaHCO_3$) and purification, the formal $[\pi 4_s+\pi 2_s]$-cycloaddition product **23** in 56% yield. The allenyl compound **26**, formed by a propargyl-allenyl rearrangement, could not be detected. The phenyl precursors **15** and **16** (entries 2 and 3) reacted in a similar way to give the 3,4-dihydro-2*H*-1,3-oxazin-2-ones **24** and **25** in 48% and 13%, respectively. The low yield of **25** is likely due to very slow formation of the iminium ion, which is destabilized by the *p*-nitrophenyl function.

In the ^1H NMR spectrum of **23** in $CDCl_3$ a singlet was found at 4.59 ppm which integrated for two hydrogens. Apparently, H^4 and H^5 have the same chemical shift in $CDCl_3$. A spectrum of **23** in C_6D_6 showed an AB system for H^4 (4.30 ppm) and H^5 (4.51 ppm) with a coupling constant of 4.0 Hz. Compound **24** also showed this coincidence ($CDCl_3$: 4.63 ppm; C_6D_6: H^4 4.22 ppm (J = 4.1 Hz), H^5 4.47 ppm (J = 4.1 Hz). Oxazine **25**, however, showed doublets for H^4 and H^5 in $CDCl_3$ (H^4: 4.62 ppm (J = 4 Hz), H^5: 4.80 ppm (J = 4 Hz)).

The formation of the products depends on the nature of the Lewis acid and the solvent used. When the reaction was induced by ethylaluminium dichloride (entry 4), a 75:25 mixture of **23** and allenyl compound **26** was formed. Using benzene as solvent (entry 5), allene **27** was the major product formed. The allenes exhibited highly characteristic ^1H NMR data. For instance, allene **26** showed a quartet (J = 7 Hz) at 5.42 ppm for the vinylic methine hydrogen and a doublet of doublets (J = 7, 2 Hz) at 4.57 ppm for the $=CH_2$ hydrogens. *tert*-Butyl carbamate **17** (entry 6) reacted more cleanly, compared to the ethyl compounds **14-16** to give oxazinone **23** in a higher yield (67%). Apparently, benzyl carbamate **18** (entry 7) is easily deprotected under the reaction conditions because allenic amine **28** was formed besides oxazinone **23** (69%, ratio 23:77). Formation of the *N*-ethoxycarbonyl-iminium ion from precursor **19** proceeded rapidly, because of the electron-donating property of

Table 2. Reaction of the Precursors with Propargyltrimethylsilane **1** (3 equiv, 0 °C → r.t.)

entry	precursor	solvent	Lewis acid (1.2 equiv)	product(s) (isolated yield, product ratio)
				 **23** X = OMe **24** X = H **25** X = NO_2
				 **26** R = CO_2Et, X = OMe **27** R = CO_2Et, X = H **28** R = H, X = OMe
1	**14**	CH_2Cl_2	$SnCl_4$	**23** (56%)
2	**15**	CH_2Cl_2	$SnCl_4$	**24** (48%)
3	**16**	CH_2Cl_2	$SnCl_4$	**25** (13%)[a]
4	**14**	CH_2Cl_2	$EtAlCl_2$	**23**, **26** (63%, 75:25)[b]
5	**15**	C_6H_6	$EtAlCl_2$	**24**, **27** (45%, 34:66)[b]
6	**17**	CH_2Cl_2	$EtAlCl_2$	**23** (67%)
7	**18**	CH_2Cl_2	$EtAlCl_2$	**23**, **28** (69%, 77:23)
				 **29**  **30**
8	**19**	CH_2Cl_2	$EtAlCl_2$	**29**, **30** (52%, 50:50)[b]
				 **31**  **32**
9	**21**	CH_2Cl_2	$SnCl_4$	**31**, **32** (26%, 42:58)
				 **33**  **34**
10	**22**	CH_2Cl_2	$TiCl_4$	**33**, **34** (44%, 75:25)[b]

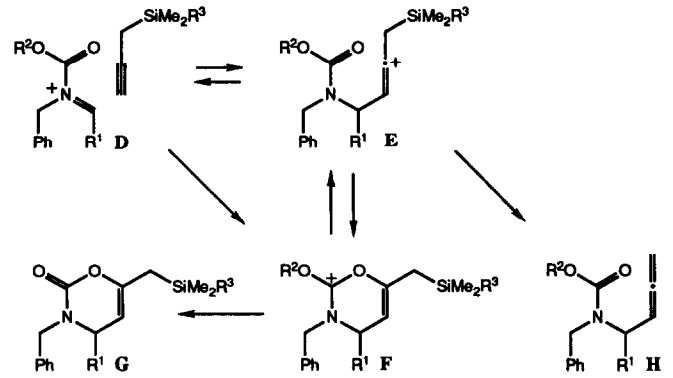
[a] Oxazinone **25** was contaminated with ethyl *N*-benzylcarbamate, which results from hydrolysis of the precursor.
[b] These products could not be separated by flash chromatography; ratio estimated by ^1H NMR.

the furfuryl moiety. The reactivity, on the contrary, was low (vide infra). Reaction of **19** (entry 8) with $EtAlCl_2$ gave a 50:50 mixture of **29** and **30**. Upon treatment with $SnCl_4$, precursor **21** (entry 9) gave the oxazinone **31** and the allenyl compound **32** in 11% and 15%, respectively. The *N*-*p*-methoxyphenyl precursor **22** (entry 10) gave no oxazinone or allenyl compound upon treatment with **1**, but a 75:25 mixture of tetrahydro- and dihydroisoquinolines **33** and **34** in 44% yield.

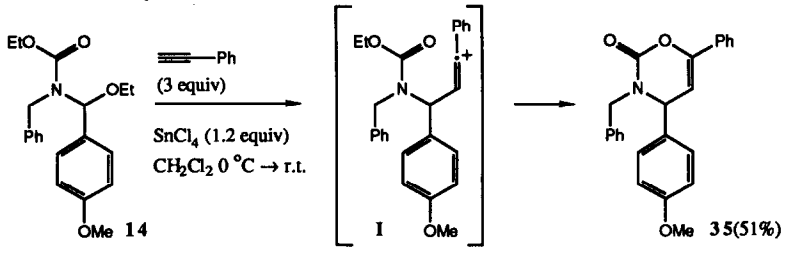
MECHANISM OF OXAZINONE VERSUS ALLENE FORMATION

For the formation of oxazinone **G** (Scheme 1), two mechanistic extremes can be envisaged, namely a concerted $[\pi 4_s + \pi 2_s]$-cycloaddition (**D** → **F** → **G**) as described[22] for the reaction of *N*-acyliminium ions with alkenes, and a stepwise mechanism[23] with the initial formation of the β-silyl stabilized cation **E** which is trapped by the carbamate carbonyl group[24,25] to give **F**. Intermediate **F** is transformed to oxazinone **G** during the reaction, or alternatively, **F** is trapped by a nucleophile (probably Cl^-) and hydrolyzed during work-up. The allenyl compound **H** is formed from β-silyl cation **E** by loss of the trimethylsilyl group.

Scheme 1

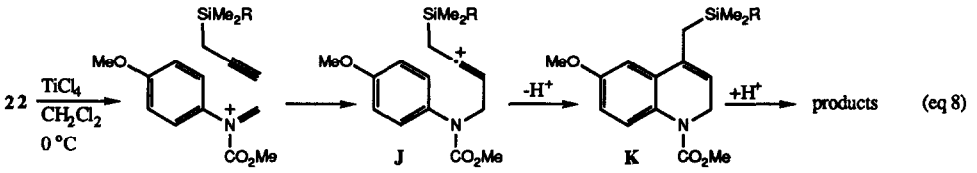


The significance of **E** as intermediate is evidenced by the following observations. First, allenyl compound **H** was formed together with oxazinone **G** in some cases (Table 2, entries 4, 5 and 7-9) indicating the importance of a cationic intermediate. Second, 1-pentyne, lacking the β-cation stabilizing silicon substituent, did not react with **14** under the same reaction conditions ($SnCl_4$, CH_2Cl_2, 0 °C → r.t.), making a purely concerted mechanism unlikely. On the other hand, **14** (eq 7) did react with phenylacetylene to furnish oxazinone **35** (51%) with a phenyl substituted vinylic cation **I** as stabilized intermediate.

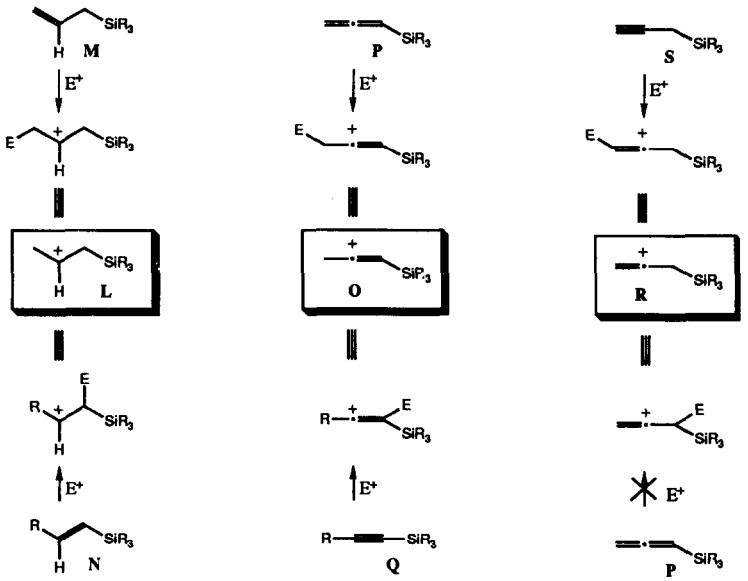


(eq 7)

A mechanistically informative result was provided by the reaction of precursor **22** (Table 2, entry 10). Treating **22** with $TiCl_4$ and propargyltrimethylsilane gave cation **J** as intermediate (eq 8, R = Me). This cation was not attacked by the carbamate moiety but by the aryl group to give allylsilane **K** (R = Me). Protodesilylation of **K**, during the reaction, produced a mixture of tetrahydro- and dihydroisoquinolines **33** and **34**.

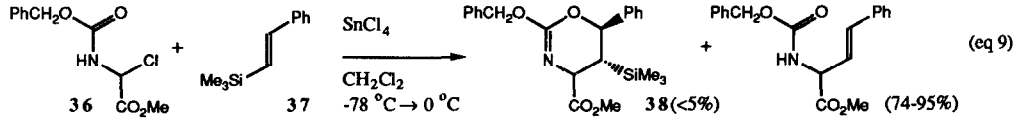


There exists extensive literature precedent describing the interception of a carbocation stabilized by a β-silicon atom. In principle, three types of carbocations with a β-silicon substituent can be distinguished, namely **L**, **O** and **R** (Scheme 2).



Scheme 2a **Scheme 2b** **Scheme 2c**

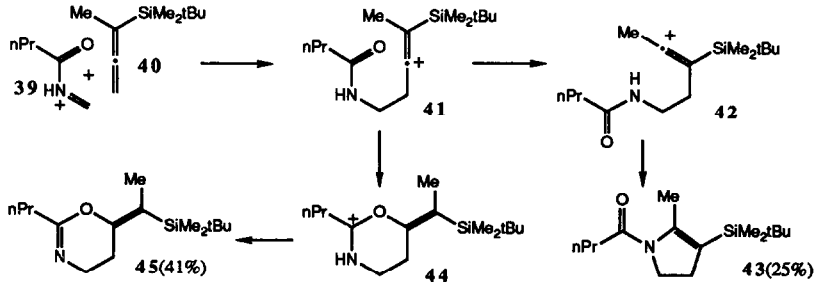
Cation **L** (Scheme 2a) is an intermediate in the reaction of an electrophile with allylsilane **M**[26,27] or vinylsilane **N**.[28] An example of the former type is the sila-Wagner-Meerwein rearrangement of the β-silyl cation, formed from conjugate addition of allyltrimethylsilane to enones, which eventually leads to cyclopentanes.[27a] The latter type is exemplified with the reaction of *N*-benzyloxycarbonyliminium ion precursor **36** (eq 9) with vinylsilane **37** to give oxazine **38** as a minor product.[28]



Vinylic cation **O** (Scheme 2b) may originate from allenylsilane **P**[26,29] or alkynylsilane **Q**.[26,30] The so-called (trimethylsilyl)cyclopentene annulation[29] involves the reaction of allenylsilanes with electron deficient systems such as electron-poor olefins,[29b-e] aldehydes,[29f] *N*-acylimines[29f] and tropylium tetrafluoroborate[29g] to

form functionalized cyclopentenes. Reaction of *N*-acyliminium ion **39** (Scheme 3) with allenylsilane **40** furnishes pyrroline **43**. Presumably after formation of the initial intermediate **41**, a 1,2-shift of the *tert*-butyldimethylsilyl group occurs to afford isomeric vinylic cation **42**, which is intercepted by the nitrogen atom to produce **43**. Interception of cation **41** by the amide carbonyl function gives cation **44**, which loses a proton to furnish oxazine **45** in 41% yield. When, in general, allenyltrimethylsilane is used as reactant, this 1,2-shift does not occur and propargyl compounds are predominantly formed.[29h]

Scheme 3

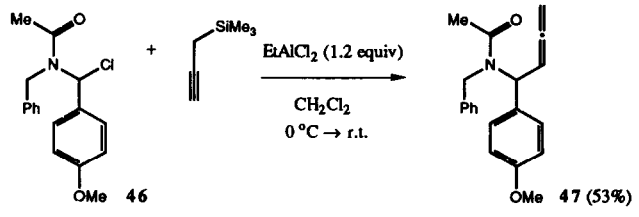


Formation of cation **O** from an alkynylsilane[26,30] was found to occur[30] in the reaction of *N*-phenylsulfoximidoyl chloride with 1-trimethylsilyl-1-propyne. Here, cation **O** is intercepted by an aromatic nucleus.

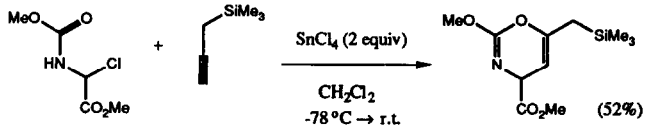
Reaction of an electrophile with propargylsilane **S** (Scheme 2c) affords the afore-mentioned vinylic cation **R** (Scheme 1). Species **R** was reported to be an intermediate also in the reaction of propargylsilanes with some acetals to give dihydrofurans in addition to the desired allenes.[3] Cation **R** cannot be formed from allenylsilane **P**, because this process cannot compete with formation of **O** (Scheme 2b).[29a]

SUBSTRATE INFLUENCE ON THE OXAZINONE/ALLENE RATIO

The formation of oxazinone **G** at the expense of allene **H** (Scheme 1) can in principle be promoted by two factors. First, a better leaving group R^2 (such as a *tert*-butyl or benzyl group) in the carbamate moiety should accelerate the formation of **G** from **F**. Second, a sterically more hindered propargylsilane (one methyl group on the silicon atom substituted by a bulky alkyl group) should lead to a longer lifetime of the vinylic cationic intermediate **E** by retarding the loss of the silyl group through nucleophilic attack, thus favouring the step from **E** to **F**.



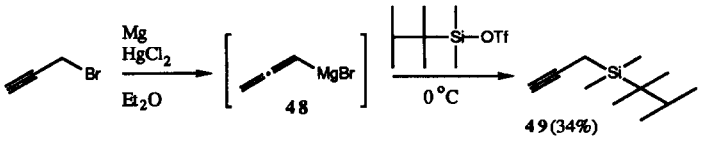
(eq 10)



(eq 11)

That *tert*-butyl carbamate **17** gives a higher yield than its ethyl analogue **14** in reaction with trimethylpropargylsilane (Table 2 entries 1 and 6) can be ascribed to the fact that the *tert*-butyl group from intermediate **F**

(Scheme 1, R^1 = *p*-methoxyphenyl, R^2 = *t*-Bu, R^3 = Me) is easily lost to form isobutene. The result with benzyl carbamate **18** (entry 7) also shows that in this case the nitrogen is readily deprotected. On the contrary, formation of an allenic product should be favoured upon replacing the carbamate functionality by an amide function, thus preventing the oxazine route. *N*-Acetyl compound **46** (eq 10) was generated *in situ* by addition of acetyl chloride to imine **10**. Reaction of **46** with propargyltrimethylsilane under the influence of $EtAlCl_2$ indeed gave allene **47** in 53% yield. An oxazine can also not be formed in this case due to the presence of the *N*-benzyl substituent (cf. Scheme 3, **44** → **45**). An example[31] of the formation of an oxazine is depicted in eq 11 (see also eq 9).



(eq 12)

To prepare a propargylsilane with a bulky R group on silicon, the reaction of the Grignard reagent **48** derived from propargyl bromide[32] (eq 12) with the appropriate trialkylsilyl halide was investigated.[6] Probably due to steric hindrance, *tert*-butyldimethylsilyl chloride did not react with **48** even under reflux conditions. The more reactive dimethylthexylsilyl triflate did react with **48** to give silane **49** in 34% yield.[33]

Table 3.

entry	precursor	Lewis acid (1.2 equiv)[a]	alkyne or alkene compound (3.0 equiv)	product (isolated yield)
1	**14**	$SnCl_4$	**49**	**50** (79%)
2	**22**	$TiCl_4$	**49**	**51** (28%)
3	**14**	$EtAlCl_2$	**52**	**53** (97%)
4	**19**	$EtAlCl_2$	**52**	**54** (46%)

[a] Conditions: CH_2Cl_2, 0 °C → r.t.

Dimethylpropargylthexylsilane **49** (Table 3, entry 1) reacted cleanly with **14** to give oxazinone **50** in good yield (79%). This result indicates that the intermediate vinylic cation (Scheme 1, R^1 = *p*-methoxyphenyl, R^2 = Et, R^3 = thexyl) has a longer lifetime, because of the fact that the silicon atom is sterically more hindered due to the presence of the thexyl group. Nucleophilic attack on the silicon atom apparently cannot compete with cation capture.[34] This is confirmed by the reaction of precursor **22** with **49** (entry 2). In this case the only isolated product was α-silyl ketone **51** (28%), formed through hydrolysis of the intermediate cation **J** (eq 8, R = thexyl).

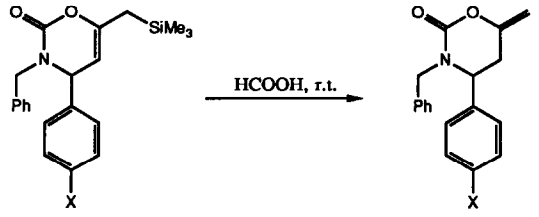
To test whether the carbamate function can intercept the β-silyl cation **L** (Scheme 2a), formed during the reaction of an *N*-alkoxycarbonyliminium ion with allyltrimethylsilane **52**, precursors[35] **14** and **19** were examined. Reaction of precursor **14** gave, however, only allyl compound **53** in almost quantitative yield (Table 3, entry 3). Because of the low reactivity of the *N*-alkoxycarbonyliminium ion derived from **19**, product **54** was isolated in a rather low yield (46%).

CHEMICAL PROPERTIES OF THE ALLYLSILANES 23 AND 24

The compounds **23-25**, **29** and **31** feature two interesting functionalities, namely the oxazinone ring system and the allylsilane moiety. Although the 1,3-oxazin-2-one ring system is well-known in the literature,[36] only a limited number of 3,4-dihydro-2*H*-1,3-oxazin-2-ones have been described. All of the syntheses make use of an isocyanate as reactant. Reaction of enones[37a] with chlorosulfonyl isocyanate (CSI) produces this ring system.[37b] An intramolecular variant is the reaction of ketones with isocyanates, obtained either via Curtius rearrangement of acyl azides[38] or via reaction of amines with phosgene.[39]

Allylsilanes with an oxygen substituent β to silicon have been described in the literature.[40] The reactivity, however, of the allylsilane functionality has not been described until recently.[41]

The chemical properties of the allylsilane moiety in the oxazinones **23** and **24** were investigated in some detail. Protodesilylation of the allylsilane funtionality in **23** and **24** occurred by stirring these compounds in formic acid to afford the 6-methylene-1,3-oxazin-2-ones[42] **55** and **56** in almost quantitative yields (eq 13).

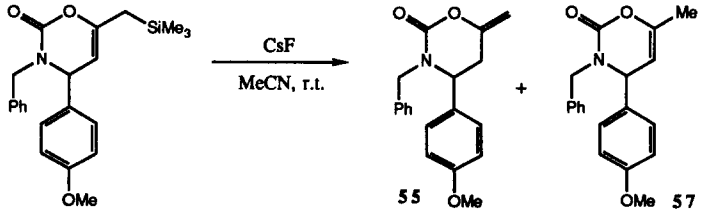


23 X = OMe
24 X = H

55 X = OMe (95%)
56 X = H (96%)

(eq 13)

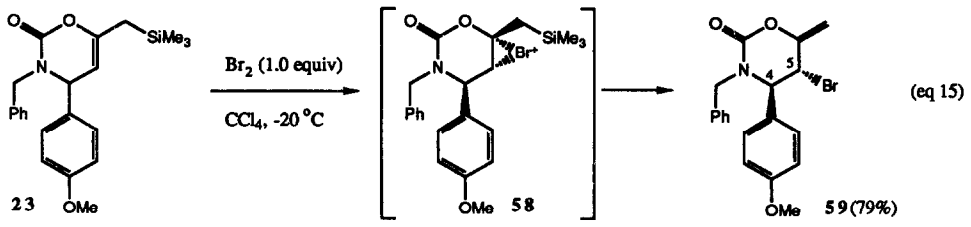
Removal of silicon from **23** through reaction with cesium fluoride in acetonitrile gave an inseparable 20:80 mixture of **55** and **57** in 84% yield (eq 14). The mechanism of fluoride-mediated desilylation involves the formation of allyl anions, so that the regioselectivity is largely controlled by thermodynamic factors.[43]



23

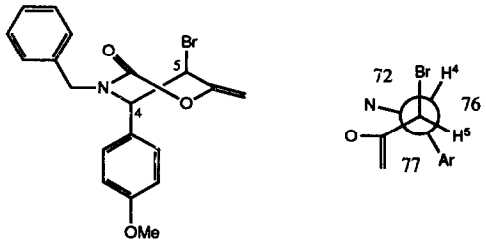
55:**57** = 20:80 (84%)

(eq 14)



(eq 15)

Treatment of **23** with bromine (eq 15)[44] furnished isomerically pure **59** as a crystalline compound (mp 130-131 °C) in 73% yield. The coupling constant between the ring protons at C-4 and C-5 in **59** is 1.5 Hz. This value did not allow an immediate conclusion on the stereochemical relationship of the stereocentres at C-4 and C-5. It is known from the literature[45] that oxazinones of type **59** prefer to have the phenyl group at C-4 in a pseudo-axial orientation, because of steric repulsion[46] between the aryl group at C-4 and the *N*-alkyl substituent. When the C-4 and C-5 substituents are both in a pseudo-axial orientation (*trans*-compound), the dihedral angle between the protons at C-4 and C-5 is expected to be about the same as in the case of a *cis*-relationship, with one pseudo-axial and one pseudo-equatorial substituent. The *trans*-relationship in **59** was secured by an X-ray crystallographic analysis the result of which is depicted in Figure 1. Both substituents at C-4 and C-5 are in a pseudo-axial orientation. The dihedral angle of 76° is well in accord with the coupling constant *J* (H^4, H^5) of 1.5 Hz. The crystal structure[47] of 4,4,6-trimethyl-3,4-dihydro-2*H*-1,3-oxazin-2-one shows that the 3,4-dihydro-2*H*-1,3-oxazin-2-one ring system is almost planar. Bromine, therefore, will attack the double bond in **23** (eq 15) from the less hindered side to give via bromonium ion **58** the *trans*-bromide **59**.



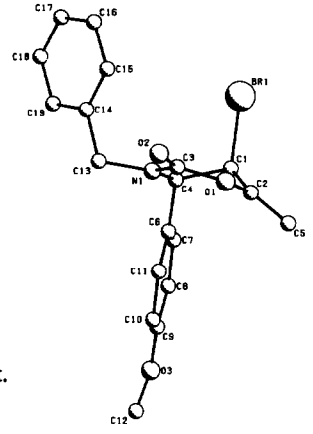
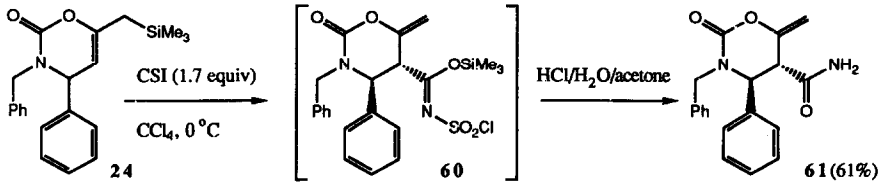


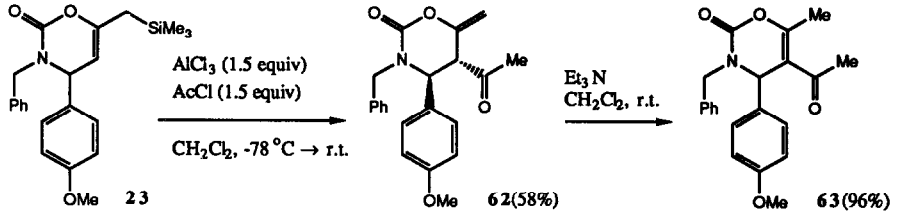
Figure 1. Conformation and dihedral angles about the C4-C5 bond of oxazinone **59** based on the X-ray crystal structure shown right.

The strong electrophile chlorosulfonyl isocyanate (CSI) was examined next. Stirring **24** with CSI[44] (eq 16) in carbon tetrachloride and subsequent hydrolysis of intermediate **60** produced primary amide **61** (mp 170-171 °C) in 61% yield. The coupling constant *J* (H^4, H^5) of 1.5 Hz points to a *trans*-relationship between the substituents.



(eq 16)

Reactions of **23** with acid chlorides were not always successful. The titanium tetrachloride (2 equiv) induced reaction of **23** with acetyl chloride (2 equiv, CH_2Cl_2, -78 °C) afforded a 50:50 mixture of starting material and protodesilylated product **55** (eq 13), caused by traces of HCl in the reaction mixure. When the more reactive Lewis acid aluminium trichloride (1.5 equiv) was used (AcCl, CH_2Cl_2, -78 °C),[48] *trans*-acetyl compound **62** (eq 17) was isolated in 58% yield. The *trans*-relationship was again confirmed by the coupling constant J (H^4, H^5) of 1.5 Hz. The exocyclic double bond in **62** was brought into conjugation with the ketone by treating **62** with triethylamine to give 3,4-dihydro-2*H*-1,3-oxazin-2-one **63** (96%).



(eq 17)

CONCLUSIONS

The reaction of *N*-alkoxycarbonyliminium ion **D** (Scheme 1) with propargylsilane **1** proceeds by a stepwise mechanism involving β-silyl cation **E** to form oxazinone **G** as the major product. The allylsilane moiety in oxazinone **G** reacts with electrophiles as a normal allylsilane to give the electrophilic substitution products with double bond shift (eq 13, 15-17).

ACKNOWLEDGEMENT

K. Goubitz and D. Heijdenrijk of the Department of Crystallography are kindly acknowledged for the X-ray crystal structure determination. We thank C. Kruk and his staff for their help in obtaining and interpreting the NMR spectra. This work was supported by the Netherlands Foundation for Chemical Research (SON) with the financial aid from the Netherlands Organization for Advancement of Pure Research (NWO).

EXPERIMENTAL

General information. For general information see also ref 49. $TiCl_4$ and $SnCl_4$ were distilled and stored under a dry nitrogen atmosphere, $TiCl_4$ as a 1.0 M solution and $SnCl_4$ as a 1.2 M solution in CH_2Cl_2. Dry Et_2O was distilled under an atmosphere of dry nitrogen from sodium benzophenone ketyl prior to use. Dry EtOH was distilled from $Mg(OEt)_2$ prior to use. Dry DMF was distilled from CaH_2 and stored under an atmosphere of dry nitrogen. $EtAlCl_2$ (a 1.8 M solution in toluene), allyltrimethylsilane, CSI, diethyl and di-*tert*-butyl pyrocarbonate were purchased from Aldrich. Dibenzyl pyrocarbonate, propargyl bromide, phenylacetylene, dimethylthexylsilyl triflate were purchased from Fluka. Propargyltrimethylsilane was purchased from Fluka or prepared according to a literature procedure.[6]

Ethyl *N*-benzyl-*N*-[ethoxy(4-methoxyphenyl)methyl]carbamate (14). Under a dry nitrogen atmosphere, $(EtOCO)_2O$ (1.00 mL, 6.97 mmol) was added to a solution of *N*-4-methoxybenzylidenebenzylamine **10**[19a] (1.30 g, 5.77 mmol) in 50 mL of EtOH. The reaction mixture was heated for 17 h at 60-70 °C and then cooled and concentrated *in vacuo*. The residue was chromatographed to give **14** (1.66 g, 4.83 mmol, 84%) as a colourless oil. R_f 0.60 (EtOAc/hexane: 1/4). IR 2840 (OMe), 1685 (NC=O). ^1H NMR (100 MHz) 1.08 (t, J = 7 Hz, 3 H, $CHOCH_2CH_3$), 1.22 (bt, J = 7 Hz, 3 H, $OCOCH_2CH_3$), 3.47 (bq, J = 7 Hz, 2 H, $CHOCH_2CH_3$), 3.78 (s, 3 H, OCH_3), 3.96 (d, J = 16 Hz, 1 H, CHPh), 4.21 (bq, J = 7 Hz, 2 H, $OCOCH_2CH_3$), 4.36 (d, J = 16 Hz, 1 H, CHPh), 6.50 (bs, 1 H, NCHO), 6.8-7.5 (m, 9 H, Ph and C_6H_4OMe). ^{13}C NMR (50 MHz) 14.4 (2 × CH_3), 45.3 (NCH_2), 55.0 (OCH_3), 61.4 ($COOCH_2$), 63.2 (OCH_2), 85.3 (NCHO), 113.4, 126.3, 127.5, 126.6, 130.8, 139.0, 156.9 (b, NC=O), 159.2.

Ethyl *N*-benzyl-*N*-(ethoxyphenylmethyl)carbamate (15). Under a dry nitrogen atmosphere, $(EtOCO)_2O$ (0.390 mL, 2.65 mmol) was added to a solution of *N*-benzylidenebenzylamine **11**[19b] (433 mg, 2.22 mmol) in 10 mL of EtOH. The reaction mixture was heated for 24 h at 60-70 °C. The cooled reaction mixture was concentrated *in vacuo*. The residue was chromatographed to give **15** (570 mg, 1.83 mmol, 82%) as a colourless oil. R_f 0.55 (EtOAc/hexane: 1/4). IR 1685 (NC=O). ^1H NMR (100 MHz) 1.10 (t, J = 7 Hz, 3 H, $CHOCH_2CH_3$), 1.24 (bt, J = 7 Hz, 3 H, $OCOCH_2CH_3$), 3.50 (bq, J = 7 Hz, 2 H, $CHOCH_2CH_3$), 3.94 (d, J = 16 Hz, 1 H, CHPh), 4.12 (q, J = 7 Hz, 2 H, $OCOCH_2CH_3$), 4.37 (bd, J = 16 Hz, 1 H, CHPh), 6.57 (bs, 1 H, CHOEt), 7.0-7.5 (m,

10 H, 2 × Ph). ^{13}C NMR (63 MHz) 14.6 (2 × CH_3), 45.6 (NCH_2), 61.6 ($COOCH_2$), 63.4 (OCH_2), 85.6 (NCHO), 126.5 (2 × C), 127.7, 127.9, 128.1, 138.8, 139.0, 157.5 (b, NC=O).

Ethyl *N*-benzyl-*N*-[ethoxy(4-nitrophenyl)methyl]carbamate (16). Under a dry nitrogen atmosphere, $(EtOCO)_2O$ (0.750 mL, 5.09 mmol) was added to a solution of *N*-4-nitrobenzylidenebenzylamine **12**[19c] (1.00 g, 4.16 mmol) in 15 mL of EtOH. The reaction mixture was heated for 24 h at 60-70 °C. Additional $(EtOCO)_2O$ (0.60 mL, 4.07 mmol) was added and stirring continued for another 24 h at 60-70 °C. The reaction mixture was cooled and concentrated *in vacuo*. The residue was chromatographed to give **16** (0.760 g, 2.12 mmol, 51%) as a colourless oil. R_f 0.60 (EtOAc/hexane: 1/4). IR 1685 (NC=O), 1520 and 1345 (NO_2). ^{1}H NMR (200 MHz) 1.12 (t, J = 7 Hz, 3 H, $CHOCH_2CH_3$), 1.23 (t, J = 7 Hz, 3 H, $OCOCH_2CH_3$), 3.52 (m, 2 H, $CHOCH_2CH_3$), 4.02 (d, J = 15 Hz, 1 H, CHPh), 4.25 (m, 3 H, $OCOCH_2CH_3$ and CHPh), 6.50 (bd, two rotamers, 1H, OCHN), 7.10 (m, 5H, Ph), 7.56 (d, J = 7.5 Hz, 2 H), 8.09 (d, J = 7.5 Hz, 2 H).

***tert*-Butyl *N*-benzyl-*N*-[ethoxy(4-methoxyphenyl)methyl]carbamate (17).** Under a dry nitrogen atmosphere, $(t\text{-BuOCO})_2O$ (1.00 mL, 4.35 mmol) was added to a solution of *N*-4-methoxybenzylidenebenzylamine **10**[19a] (0.496 g, 2.20 mmol) in 10 mL of EtOH. The reaction mixture was heated for 24 h at 60-70 °C, then cooled and concentrated *in vacuo*. The residue was chromatographed to give **17** (0.657 g, 1.77 mmol, 80%) as a colourless oil. R_f 0.55 (EtOAc/hexane: 1/6). IR 2840 (OMe), 1680 (NC=O). ^{1}H NMR (100 MHz) 1.09 (bt, J = 7 Hz, 3 H, OCH_2CH_3), 1.43 (s, 9 H, $C(CH_3)_3$), 3.51 (m, 2 H, OCH_2CH_3), 3.78 (s, 3 H, OCH_3), 3.87 (d, J = 16 Hz, 1 H, CHPh), 4,28 (bd, J = 16 Hz, 1 H, CHPh), 6.49 (bs, 1 H, CHN), 6.7-7.5 (m, 9 H, Ph and C_6H_4OMe).

Benzyl *N*-benzyl-*N*-[ethoxy(4-methoxyphenyl)methyl]carbamate (18). Under a dry nitrogen atmosphere, $(PhCH_2OCO)_2O$ (0.661 g, 2.31 mmol) was added to a solution of *N*-4-methoxybenzylidenebenzylamine **10**[19a] (0.406 g, 1.80 mmol) in 10 mL of EtOH. The reaction mixture was heated for 24 h at 60-70 °C, then cooled and concentrated *in vacuo*. The residue was chromatographed twice (EtOAc/hexane: 1/4 and EtOAc/hexane: 1/7) to give **18** (0.403 g, 0.994 mmol, 55%) as a colourless oil. R_f 0.60 (EtOAc/hexane: 1/4). IR 2840 (OMe), 1685 (NC=O). ^{1}H NMR (100 MHz) 1.06 (bt, J = 7 Hz, 3 H, OCH_2CH_3), 3.50 (m, 2 H, OCH_2CH_3), 3.79 (s, 3 H, OCH_3), 3.98 (d, J = 16 Hz, 1 H, CHPh), 4.37 (bd, J = 16 Hz, 1 H, CHPh), 5.20 (bs, 2 H, OCH_2Ph), 6.55 (bs, 1 H, NCHO), 6.7-7.5 (m, 14H, 2 × Ph and C_6H_4OMe).

Ethyl *N*-benzyl-*N*-[ethoxy(2-furyl)methyl]carbamate (19). Under a dry nitrogen atmosphere, $(EtOCO)_2O$ (0.240 mL, 1.63 mmol) was added to a solution of *N*-furfurylidenebenzylamine **13**[19d] (0.255 g, 1.37 mmol) in 10 mL of EtOH. The reaction mixture was stirred for 1 h at room temperature and then concentrated *in vacuo*. The residue was chromatographed to give **19** (0.398 g, 1.31 mmol, 96%) as a colourless oil. R_f 0.55 (EtOAc/hexane: 1/4). IR 1690 (NC=O). ^{1}H NMR (100 MHz) 1.12 (t, J = 7 Hz, 3 H, $CHOCH_2CH_3$), 1.30 (bt, J = 7 Hz, 3 H, $COOCH_2CH_3$), 3.52 (bq, J = 7 Hz, 2 H, $CHOCH_2CH_3$), 4.16 (d, J = 16 Hz, 1 H, CHPh), 4.20 (bq, J = 7 Hz, 2 H, $COOCH_2CH_3$), 4.47 (d, J = 16 Hz, 1 H, CHPh), 6.28 (dd, J = 3, 2 Hz, 1 H, furfuryl H^4), 6.40 (d, J = 3 Hz, 1 H, furfuryl H^3), 6.52 (s(b), 1 H, NCH), 7.16 (m, 5 H, Ph), 7.26 (d, J = 2 Hz, 1 H, furfuryl H^5).

Methyl *N*-benzyl-*N*-(methoxymethyl)carbamate (21). Under a dry nitrogen atmosphere, a 55% NaH dispersion in mineral oil (1.30 g, 29.8 mmol) was washed (3 ×) with 5 mL of hexane, and 60 mL of DMF was added. Methyl *N*-benzylcarbamate **20**[21] (4.00 g, 24.2 mmol) was added in 10 portions in 10 min at room temperature. The mixture was stirred for 0.5 h, then a solution of chloromethyl methyl ether (2.0 mL, 26.3 mmol) in 10 mL of DMF was then added dropwise. After stirring overnight, the reaction mixture was poured out into 750 mL of water and extracted (4 ×) with 200 mL ether/pentane (1:1). The combined extracts were washed with 100 mL of water, dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed to give **21** (2.29 g, 10.9 mmol, 45%) as a light-yellow oil. R_f 0.75 (EtOAc/hexane: 1/4). IR 1700 (NC=O). ^{1}H NMR (200 MHz) 3.31 (bs, 3 H, CH_2OCH_3), 3.77 (s, 3 H, $COOCH_3$), 4.54 (bs, 2 H, $PhCH_2N$), 4.66 (s) and 4.74 (s, two rotamers, 2 H, NCH_2O), 7.30 (m, 5 H, -Ph).

Methyl *N*-(methoxymethyl)-*N*-(4-methoxyphenyl)carbamate (22). At 0 °C, methyl chloroformate (2.85 mL, 36.9 mmol) was added dropwise to a solution of *p*-methoxyaniline (4.55 g, 36.9 mmol) in 15 mL of pyridine. The mixture was allowed to warm up to room temperature and stirred for 2 days. The mixture was poured out into 1 N HCl and extracted with chloroform (3 ×). The organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*, to give methyl *N*-(4-methoxyphenyl)carbamate (6.02 g, 33.2 mmol, 90%) as a light-purple crystalline solid, mp 88-89 °C (hexane/EtOAc, Lit[50] 88 °C). IR 2840 (OMe), 1730 (CO). ^{1}H NMR (100 MHz) 3.73 (s, 3 H, $COOCH_3$), 3.76 (s, 3 H, $C_6H_4OCH_3$), 6.65 (s(b), 1 H, NH), 6.78-6.85 (m, 2 H, 2 × H^3), 7.20-7.30 (m, 2 H, 2 × H^2). A 55-60% dispersion of NaH (134 mg, 3.07 mmol) in mineral oil was washed (3 ×) with 4 mL of hexane under a dry nitrogen atmosphere and then 2 mL of DMF was added. A solution of methyl *N*-(4-methoxyphenyl)carbamate (0.503 g, 2.78 mmol) in 8 mL of DMF was added dropwise at 0 °C. The mixture was stirred for 1 h and then a solution of chloromethyl methyl ether (0.30 mL, 4.0 mmol) in 2 mL of DMF was added dropwise. After 20 min the reaction mixture was warmed up to room temperature and stirred for 18 h. The mixture was poured out into water and extracted with CCl_3CH_3 (3 ×) and the extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed to give **22** (0.552 g, 2.45 mmol, 88%) as a colourless oil. R_f 0.30 (EtOAc/hexane: 1/4). IR 1705 (NC=O). ^{1}H NMR (200 MHz) 3.39 (s, 3 H, CH_2OCH_3), 3.68 (s(b), 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 4.94 (s, 2 H, CH_2OCH_3), 6.8-6.9 (m, 2 H), 7.1-7.3 (m, 2 H).

General procedure A: Reaction of α-alkoxycarbamates with propargylsilanes, induced by $SnCl_4$. Under a dry nitrogen atmosphere, 3 equiv of silane were added to a stirred 0.1 M solution of the α-alkoxycarbamate in CH_2Cl_2. At 0 °C, 1.2

equiv of a 1.2 M solution of $SnCl_4$ in CH_2Cl_2 was added dropwise, and stirring continued for 1 h. After warming up to room temperature and stirring for 3 h, the reaction mixture was diluted with $CHCl_3$ and poured into saturated aq $NaHCO_3$. The mixture was stirred vigourously for 15 min, then filtered over celite and extracted with $CHCl_3$ (4 ×). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed.

General procedure B: Reaction of α-alkoxycarbamates with propargyltrimethylsilane and allyltrimethylsilane induced by $EtAlCl_2$. Under a nitrogen atmosphere, propargyltrimethylsilane or allyltrimethylsilane (3 equiv) and a 1.8 M solution of $EtAlCl_2$ (in toluene), respectively were added to a 0.1 M solution of the α-alkoxycarbamate in CH_2Cl_2 at 0 °C. After 1 h, the reaction mixture was allowed to warm up to room temperature and stirring was continued for 3 h. The reaction mixture was diluted with $CHCl_3$ and poured out into saturated aq $NaHCO_3$. After extraction with $CHCl_3$ (4 ×), the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed.

3-Benzyl-4-(4-methoxyphenyl)-6-(trimethylsilylmethyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (23). According to procedure A, carbamate **14** (1.66 g, 4.84 mmol) was treated with propargyltrimethylsilane (2.20 mL, 14.5 mmol) and a 1.2 M solution of $SnCl_4$ in CH_2Cl_2 (4.80 mL, 5.76 mmol) to give **23** (1.03 g, 2.70 mmol, 56%) as a colourless oil. R_f 0.38 (EtOAc/hexane: 1/6). IR 2840 (OMe), 1710 (NC=O), 1245 and 850 (Si-C). ^1H NMR (100 MHz) 0.10 (s, 9 H, $Si(CH_3)_3$), 1.60 (s, 2 H, CH_2SiMe_3), 3.56 (d, J = 15 Hz, 1 H, CHPh), 3.81 (s, 3 H, OCH_3), 4.59 (s, 2 H, H^4 and H^5), 5.21 (d, J = 15 Hz, 1 H, CHPh), 6.6-7.3 (m, 9 H, Ph and C_6H_4OMe). ^1H NMR (C_6D_6, 200 MHz) 0.10 (s, 9 H, $Si(CH_3)_3$), 1.43 (d, J = 2 Hz, 2 H, CH_2SiMe_3), 3.31 (s, 3 H, OCH_3), 3.58 (d, J = 15.1 Hz, 1 H, CHPh), 4.30 (d, J = 4.0 Hz, 1 H, H^4), 4.51 (d, J = 4.0 Hz, 1 H, H^5), 5.47 (d, J = 15.1 Hz, 1 H, CHPh), 6.6-7.3 (m, 9 H, Ph and C_6H_4OMe). ^{13}C NMR (63 MHz) -1.6 ($Si(CH_3)_3$), 22.5 (CH_2Si), 48.4 (NCH_2), 55.2 (OCH_3), 57.7 (C-4), 97.6 (C-5), 114.2, 127.5, 128.0, 128.2, 128.5, 132.7, 135.8, 148.5 (C-6), 150.9 (C-2), 159.8. Accurate mass 381.1761 (calcd for $C_{22}H_{27}NO_3Si$ 381.1760).

3-Benzyl-4-phenyl-6-(trimethylsilylmethyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (24). According to procedure A, carbamate **15** (430 mg, 1.37 mmol) was treated with propargyltrimethylsilane (0.62 mL, 4.2 mmol) and a 1.2 M solution of $SnCl_4$ in CH_2Cl_2 (1.4 mL, 1.7 mmol) to give **24** (231 mg, 0.657 mmol, 48 %) as a colourless oil. R_f 0.45 (EtOAc/hexane: 1/4). IR 1710 (NC=O), 1245 and 850 (Si-C). ^1H NMR (100 MHz) 0.10 (s, 9 H, $Si(CH_3)_3$), 1.60 (s, 2 H, CH_2SiMe_3), 3.56 (d, J = 15 Hz, 1 H, CHPh), 4.63 (s, 2 H, H^4 and H^5), 5.23 (d, J = 15 Hz, 1 H, CHPh), 7.1-7.5 (m, 10 H, 2 × Ph). ^1H NMR (C_6D_6, 200 MHz) 0.00 (s, 9 H, $Si(CH_3)_3$), 1.36 (s, 2 H, CH_2SiMe_3), 3.46 (d, J = 15.1 Hz, 1 H, CHPh), 4.22 (d, J = 4.1 Hz, 1 H, H^4), 4.47 (d, J = 4.1 Hz, 1 H, H^5), 5.38 (d, J = 15.1 Hz, 1 H, CHPh), 6.8-7.3 (m, 10 H, 2 × Ph). ^{13}C NMR (C_6D_6, 63 MHz), -1.5 ($Si(CH_3)_3$), 22.8 (CH_2Si), 49.1 (NCH_2), 58.9 (C-4), 97.9 (C-5), 127.1, 127.8, 128.3, 128.9, 129.2, 136.9, 141.7, 149.2 (C-6), 150.8 (C-2). Accurate mass 351.1641 (calcd for $C_{21}H_{25}NO_2Si$ 351.1654).

3-Benzyl-4-(4-nitrophenyl)-6-(trimethylsilylmethyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (25). According to procedure A, carbamate **16** (169 mg, 0.472 mmol) was treated with propargyltrimethylsilane (0.16 mL, 1.1 mmol) and a 1.2 M solution of $SnCl_4$ in CH_2Cl_2 (0.90 mL, 1.1 mmol) over 24 h. The residue was chromatographed to give an inseparable 29:71 mixture of ethyl *N*-benzylcarbamate and **25** (28.3 mg, 0.060 mmol **25**, 13%). R_f 0.40 (EtOAc/hexanes 1/5). ^1H NMR (100 MHz) 0.12 (s, 9 H, H, $Si(CH_3)_3$), 1.63 (s, 2 H, CH_2SiMe_3), 3.62 (d, J = 15 Hz, 1 H, CHPh), 4.62 (d, J = 4 Hz, 1 H, H^4), 4.80 (d, J = 4 Hz, 1 H, H^5), 5.28 (d, J = 15 Hz, CHPh), 7.10-7.50 (m, 7 H), 8.24 (d, J = 8 Hz, 2 H). MS (EI, 70 eV) 396 (M^+). Accurate mass 396.1505 (calcd for $C_{21}H_{24}N_2O_4Si$ 396.1505).

Reaction of 14 with propargyltrimethylsilane induced by $EtAlCl_2$. According to procedure B, carbamate **14** (132 mg, 0.385 mmol) was treated with propargyltrimethylsilane (0.20 mL, 1.34 mmol) and a 1.8 M solution of $EtAlCl_2$ (in toluene, 0.25 mL, 0.45 mmol) in 5 mL of CH_2Cl_2 to give an inseparable 75:25 mixture of oxazinone **23** and **ethyl *N*-benzyl-*N*-[1-(4-methoxyphenyl)-2,3-butadienyl]carbamate (26)** (93.1 mg, 0.243 mmol, 63%) as a colourless oil. R_f 0.38 (EtOAc/hexane: 1/4). ^1H NMR (100 MHz) 1.19 (t, J = 7 Hz, 3 H, CH_2CH_3), 3.84 (s, 3 H, OCH_3), 4.16 (q, J = 7 Hz, 2 H, CH_2CH_3), 4.41 (d(b), J = 2 Hz, 2 H, CH_2Ph), 4.76 (dd, J = 6, 3 Hz, 2 H, $=CH_2$), 5.42 (q, J = 7 Hz, 1 H, -CH=), 5.84 (m, 1 H, NCH), 6.8-7.4 (m, 9 H, Ph and C_6H_4OMe). ^{13}C NMR (63 MHz) 14.3 (CH_3), 48.3 (NCH_2), 55.0 (OCH_3), 58.7 (NCH), 61.2 (OCH_2), 76.8 ($=CH_2$), 89.8 (-CH=), 113.1, 126.4, 127.2, 127.8, 128.9, 131.2, 138.7, 156.5 (NC=O), 158.8, 208.6 (=C=).

Reaction of 15 with propargyltrimethylsilane induced by $EtAlCl_2$ in benzene. Under a nitrogen atmosphere, carbamate **15** (198 mg, 0.630 mmol) was treated with propargyltrimethylsilane (0.28 mL, 1.88 mmol) and a 1.8 M solution of $EtAlCl_2$ (in toluene, 0.40 mL, 0.72 mmol) in 6 mL of benzene at 5 °C to room temperature (work-up as in procedure B) to give an inseparable 34:66 mixture (93.1 mg, 0.243 mmol, 63%) of oxazinone **24** and **ethyl *N*-benzyl-*N*-(1-phenyl-2,3-butadienyl)carbamate (27)** (this compound was obtained pure, after flash chromatography, by reaction of this mixture with CSI, see synthesis **61**) as a colourless oil. R_f 0.55 (EtOAc/hexane: 1/4). IR 1955 (=•=), 1685 (NC=O). ^1H NMR (100 MHz) 1.14 (t, J = 7 Hz, 3 H, OCH_2CH_3), 4.14 (q, J = 7 Hz, 2 H, OCH_2CH_3), 4.22 (d, J = 16 Hz, 1 H, CHPh), 4.53 (d, J = 16 Hz, 1 H, CHPh), 4.57 (dd, J = 7, 2 Hz, 2 H, $=CH_2$), 5.42 (q, J = 7 Hz, 1 H, -CH=), 5.80 (m, 1 H, NCH), 7.0-7.5 (m, 10 H, 2 × Ph). ^{13}C NMR (50 MHz) 14.5 (CH_3), 48.9(b, NCH_2), 59.6 (NCH), 61.5 (OCH_2), 76.9 ($=CH_2$), 89.7 (-CH=), 126.7, 127.4, 127.7, 128.1, 128.3, 138.8, 139.5, 156.8 (NC=O), 209.0 (=C=). Accurate mass 307.1558 (calcd for $C_{20}H_{21}NO_2$ 307.1573).

Reaction of 18 with propargyltrimethylsilane induced by $EtAlCl_2$. According to procedure B, carbamate **18** (392 mg, 0.968 mmol) was treated with propargyltrimethylsilane (0.45 mL, 3.02 mmol) and $EtAlCl_2$ (1.8 M solution of in toluene, 0.70

mL, 1.26 mmol). The residue was chromatographed to give two fractions. The first fraction consisted of oxazinone **23** (197 mg, 0.516 mmol, 53%). The second fraction consisted of ***N*-benzyl-*N*-[1-(4-methoxyphenyl)-2,3-butadienyl]amine (28)** (40 mg, 0.15 mmol, 16%) as a colourless oil. R_f 0.30 (EtOAc/hexane: 1/8). IR 3390 (NH), 2820 (OMe), 1950 (=•=). ^{1}H NMR (100 MHz) 1.81 (s, 1 H, NH), 3.75 (s, 2 H, CH_2Ph), 3.79 (s, 3 H, OCH_3), 4.23 (dt, J = 7, 2 Hz, 1 H, NCH), 4.80 (dd, J = 6, 2 Hz, 2 H, $=CH_2$), 5.25 (q, J = 6 Hz, 1 H, -CH=), 6.85 (m, 2 H), 7.3 (m, 7 H). ^{13}C NMR (50 MHz) 51.2 (NCH_2), 55.3 (OCH_3), 60.3 (NCH), 76.9 ($=CH_2$), 94.6 (-CH=), 113.9, 126.9, 128.2, 128.3, 128.4, 135.1, 140.3, 158.9, 207.6 (=C=). Accurate mass 265.1448 (calcd for $C_{18}H_{19}NO$ 265.1467).

Reaction of 19 with propargyltrimethylsilane induced by $EtAlCl_2$. According to procedure B, carbamate **19** (193 mg, 0.634 mmol) was treated with propargyltrimethylsilane (0.30 mL, 2.01 mmol) and a 1.8 M solution of $EtAlCl_2$ (in toluene, 0.40 mL, 0.72 mmol) in 7 mL of CH_2Cl_2, to give an inseparable 50:50 mixture of **3-benzyl-4-(2-furyl)-6-(trimethylsilylmethyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (29)** and **ethyl *N*-benzyl-*N*-[1-(2-furyl)-2,3-butadienyl]carbamate (30)** (106 mg, 0.166 mmol **13d**, 0.166 mmol **14d**, total yield 52%) as a light brown oil. R_f 0.50 (EtOAc/hexanes: 1/4). ^{1}H NMR (100 MHz) **29**: 0.14 (s, 9 H, $Si(CH_3)_3$), 1.66 (s, 2 H, CH_2Si), 3.85 (d, J = 15 Hz, 1 H, CHPh), 4.64 (m, 1 H), 4.74 (m, 1 H), 5.23 (d, J = 15 Hz, 1 H, CHPh), 6.25 (m, 2 H, furfuryl H^3 and H^4), 7.25 (m, 6 H, Ph and furfuryl H^5); **30**: 1.20 (t, J = 7 Hz, 3 H, CH_2CH_3), 4.17 (q, J = 7 Hz, 2 H, CH_2CH_3), 4.42 (s, 2 H, CH_2Ph), 4.81 (dd, J = 6, 3 Hz, 2 H, $=CH_2$), 5.38 (q, J = 6 Hz, 1 H, -CH=), 5.95 (m, 1 H, NCH), 6.25 (m, 2 H, furfuryl H^3 and H^4), 7.25 (m, 6 H, Ph and furfuryl H^5).

Reaction of 21 with propargyltrimethylsilane, induced by $SnCl_4$. According to procedure A, carbamate **21** (358 mg, 1.71 mmol) was treated with propargyltrimethylsilane (0.70 mL, 4.70 mmol) and a 1.2 M solution of $SnCl_4$ in CH_2Cl_2 (1.70 mL, 2.04 mmol) in 5 mL of CH_2Cl_2, to give two fractions. The first fraction consisted of **3-benzyl-6-(trimethylsilylmethyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (31)** (51.0 mg, 0.185 mmol, 11%) as a light-yellow oil. R_f 0.60 (EtOAc/hexanes: 1/4). IR 1705 (NC=O), 1250 and 855 (Si-C). ^{1}H NMR (200 MHz) 0.10 (s, 9 H, $Si(CH_3)_3$), 1.58 (s, 2 H, CH_2SiMe_3), 3.67 (t, J = 1.6 Hz, 2 H, NCH_2CH=), 4.57 (s, 3 H, $PhCH_2N$ + -CH=), 7.32 (m, 5 H, -Ph). ^{1}H NMR (C_6D_6, 200 MHz) 0.04 (s, 9 H, $Si(CH_3)_3$), 1.35 (s, 2 H, CH_2SiMe_3), 3.08 (s, 2 H, NCH_2-CH=), 4.02 (t, J = 3.2 Hz, 1 H, -CH=), 4.28 (s, 2 H, CH_2Ph), 7.0 (m, 5 H, -Ph). ^{13}C NMR (50 MHz) -1.5 ($Si(CH_3)_3$), 22.8 (CH_2Si), 44.6 (NCH_2), 52.0 (C-4), 91.5 (C-5), 127.8, 128.1, 128.7, 135.8, 150.6 (C-6), 151.1 (C-2). Accurate mass: 275.1322 (calcd for $C_{15}H_{21}NO_2Si$: 275.1342). The second fraction consisted of **methyl *N*-benzyl- *N*-(2,3-butadienyl)-carbamate (32)** (57.3 mg, 0.264 mmol, 15%) as a light-yellow oil. R_f 0.70 (EtOAc/hexanes: 1/4). IR 1950 (=•=), 1685 (NC=O). ^{1}H NMR (200 MHz) 3.74 (s, 3 H, OCH_3), 3.60-3.90 (m, 2 H, NCH_2CH=), 4.48 (s, 2 H, $PhCH_2N$), 4.70-4.80 (m, 2 H, $=CH_2$), 5.00-5.15 (m, 1 H, -CH=), 7.30 (m, 5 H, -Ph). ^{13}C NMR (50 MHz) 44.7 (b, NCH_2CH=), 49.8 (b, NCH_2), 52.8 (OCH_3), 76.3 ($=CH_2$), 86.6 (-CH=), 127.3, 127.8(b), 128.5, 137.6, =C= and C=O not observed. Accurate mass 217.1113 (calcd for $C_{13}H_{15}NO_2$ 217.1123).

Reaction of 22 with propargyltrimethylsilane, induced by $TiCl_4$. Under a dry nitrogen atmosphere, propargyltrimethylsilane (0.20 mL, 1.3 mmol) was added to a solution of **22** (92.6 mg, 0.411 mmol) in 7 mL of CH_2Cl_2. At 0 °C, a 1.0 M solution of $TiCl_4$ (0.50 mL, 0.50 mmol) in CH_2Cl_2 was added dropwise. After 0.5 h the mixture was warmed up to room temperature and stirred for 4 h. The reaction mixture was diluted with chloroform and poured out into saturated aq $NaHCO_3$ and stirred vigourously for 0.25 h. After filtration over celite, the mixture was extracted with chloroform. The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed to give an inseparable 75:25 mixture of **6-methoxy-4-methylene-3,4-dihydro-1-(2*H*)-quinolinecarboxylic acid methyl ester (33)** and **6-methoxy-4-methyl-1-(2*H*)-quinolinecarboxylic acid methyl ester (34)**[51] (41.9 mg, 0.180 mmol, 44%) as a light-yellow oil. R_f 0.35 (EtOAc/hexanes: 1/6). IR 2840 (OMe), 1690 (NC=O). ^{1}H NMR (100 MHz) 2.02 (dt, appears as quartet, J = 2, 1.5 Hz, 3 H, **34** CH_3), 2.70 (tt, J = 6, 2 Hz, 2 H, **33** 2 × H^3), 3.80 (m, 8 H, **33** and **34** 2 × OCH_3 and **33** 2 × H^2), 4.98 (t, J = 2 Hz, 1H, **33** $=CH^E$), 5.57 (t, J = 2 Hz, 1 H, **33** $=CH^Z$), 6.70-6.90 (m, 1 H), 7.13 (d, J = 3 Hz, 1 H), 7.51 (d, J = 9 Hz, 1 H). ^{13}C NMR (50 MHz) **33**: 32.3 (C-3), 44.3 (C-1), 52.9 (OCH_3), 55.4 (OCH_3), 108.2, 109.9 ($=CH_2$), 114.4, 125.6, 128.4, 138.4, 155.0 (b, NC=O), 156.1 (C-6); **34**: 18.4 (CH_3), 43.2 (C-1), 52.9 (OCH_3), 55.5 (OCH_3), 109.2, 111.9, 114.1, 124.7, 131.2, 131.5, 155.0 (b, NC=O), 156.4 (C-6). MS (EI, 70 eV) 233 (M^+, 100). Accurate mass 233.1054 (calcd for $C_{13}H_{15}NO_3$ 233.1052).

3-Benzyl-4-(4-methoxyphenyl)-6-phenyl-3,4-dihydro-2*H*-1,3-oxazin-2-one (35). Under a nitrogen atmosphere, a 1.2 M solution of $SnCl_4$ in CH_2Cl_2 (0.60 mL, 0.72 mmol) was added to a solution of carbamate **14** (200 mg, 0.582 mmol) and phenylacetylene (0.20 mL, 1.82 mmol) in 5 mL of CH_2Cl_2 at 0 °C. After 30 min, the reaction mixture was allowed to warm up to room temperature and stirring was continued for 1.5 h. The reaction mixture was diluted with 10 mL of $CHCl_3$ and poured out into 15 mL of saturated aq $NaHCO_3$. The mixture was stirred vigorously for 15 min, then filtered over celite and extracted with $CHCl_3$ (4 x 25 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed to give **35** (110 mg, 0.296 mmol, 51%) as a light-yellow oil. R_f 0.21 (EtOAc/hexanes: 1/4). IR 2840 (OMe), 1705 (NC=O). ^{1}H NMR (250 MHz) 3.68 (d, 1/2 AB, 1 H, J = 15.1 Hz, CHPh), 3.81 (s, 3 H, OCH_3), 4.82 (d, J = 4.4 Hz, 1 H, H^4), 5.31 (d, 1/2 AB, 1 H, J = 15.1 Hz, CHPh), 5.55 (d, J = 4.4 Hz, H^5), 6.91 (d, J = 8.6 Hz, 2 H), 7.20 (d, J = 8.6 Hz, 2 H), 7.10-7.40 (m, 8 H), 7.60-7.70 (m, 2 H). ^{13}C NMR (50 MHz) 48.6 (NCH_2), 55.3 (OCH_3), 57.8 (C-4), 99.6 (C-5), 114.5, 124.6, 127.8, 128.3, 128.4, 128.6, 128.7, 129.3, 131.4, 131.6, 135.6, 146.6 (C-6), 150.7 (C-2), 159.9.

***N*-Benzyl-*N*-[1-(4-methoxyphenyl)-2,3-butadienyl]acetamide (47).** Under a dry nitrogen atmosphere, freshly

distilled acetyl chloride (78 µL, 1.1 mmol) was added to a solution of imine **10** (202 mg, 0.897 mmol) in 8 mL of CH_2Cl_2 and stirred for 0.5 h at room temperature. At 0 °C, propargyltrimethylsilane (0.40 mL, 2.7 mmol) and subsequently a 1.8 M solution of $EtAlCl_2$ in toluene (0.60 mL, 1.1 mmol) were added. After stirring the mixture for 1.5 h at 0 °C, it was warmed up to room temperature and stirred for 0.5 h. The reaction mixture was diluted with $CHCl_3$ and poured out into saturated aq $NaHCO_3$ and stirred vigorously for 0.25 h. The mixture was filtered over celite and extracted with $CHCl_3$ (4 ×). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed to yield **47** (145 mg, 0.472 mmol, 53%) as a light-brown oil. R_f 0.35 (EtOAc/hexane: 1/2). IR 2840 (OMe), 1955 (=•=), 1625 (NC=O). ^{1}H NMR (100 MHz) 1.9-2.4 (m, 3 H, $OCCH_3$), 3.84 (s, 3 H, OCH_3), 4.25-4.65 (m, 2 H, CH_2Ph), 4.79 (dd, 2 H, J = 6 Hz, J = 3 Hz, $=CH_2$), 5.34 (bq, J = 6 Hz, 1 H, -CH=), 6.3-7.4 (m, 10 H, Ph and C_6H_4OMe and NCH). ^{13}C NMR (50 MHz) 22.4 (CH_3), 48.8(b, NCH_2), 55.2 (OCH_3), 56.0 (b, NCH), 77.2 (b, $=CH_2$), 89.9 (b, -CH=), 113.8, 126-129 (b), 130.5 (b), 136.9 (b), 159.1 (b), 171.2 (b, NC=O), =C= not observed. Accurate mass 307.1573 (calcd for $C_{20}H_{21}NO_2$ 307.1572).

Dimethyl(2-propynyl)(1,1,2-trimethylpropyl)silane (49). Under a dry nitrogen atmosphere a solution of allenylmagnesium bromide **48** was prepared[32] from Mg (0.60 g, 25 mmol), $HgCl_2$ (25 mg, 0.092 mmol) and propargyl bromide (1.9 mL, 25 mmol) in 5 mL of Et_2O. At 0 °C a solution of dimethylthexylsilyl triflate (6.3 mL, 25 mmol) in 5 mL of Et_2O was added dropwise. The reaction mixture was stirred at room temperature for 18 h and poured into 100 mL of cold (0 °C) saturated aq NH_4Cl. After extraction with 50 mL ether (4 ×), the combined organic extracts were dried (K_2CO_3) and concentrated *in vacuo*. The residue was chromatographed to yield **49** (1.55 g, 8.51 mmol, 34%) as a colourless oil. R_f 0.80 (hexanes). IR 3300 (≡CH), 2050 (C≡C), 1245 and 840 (Si-C). ^{1}H NMR (200 MHz) 0.14 (s, 6 H, $Si(CH_3)_2$), 0.87 (d, J = 7 Hz, 6 H, $CH(CH_3)_2$), 0.87 (s, 6 H, $C(CH_3)_2$), 1.52 (d, J = 3 Hz, 2 H, CH_2), 1.62 (septet, J = 7 Hz, 1 H, $CH(CH_3)_2$), 1.82 (t, J = 3 Hz, 1 H, ≡CH). ^{13}C NMR (63 MHz) -4.2 ($Si(CH_3)_2$), 4.6 (CH_2Si), 18.6 ($(CH_3)_2$), 20.9 ($(CH_3)_2$), 23.7 (SiC), 34.8 ($CHMe_2$), 67.0 (≡C-) , ≡CH not observed.

3-Benzyl-6-[dimethyl(1,1,2-trimethylpropyl)silylmethyl]-4-(4-methoxyphenyl)-3,4-dihydro-2*H*-1,3-oxazin-2-one (50). According to procedure A, carbamate **14** (303 mg, 0.882 mmol) was treated with **49** (433 mg, 2.37 mmol) and a 1.2 M solution of $SnCl_4$ in CH_2Cl_2 (0.9 mL, 1.1 mmol) to give **50** (293 mg, 0.666 mmol, 79%) as a yellow oil. R_f 0.45 (EtOAc/hexane: 1/4). IR 2830 (OMe), 1710 (NC=O), 1245 and 840 (Si-C). ^{1}H NMR (200 MHz) 0.09 (s, 3 H, $SiCH_3$), 0.16 (s, 3 H, $SiCH_3$), 0.85 (s, 6 H, $SiC(CH_3)_2$), 0.87 (d, J = 7 Hz, 6 H, $CH(CH_3)_2$), 1.62 (septet, J = 7 Hz, 1 H, $CHMe_2$), 1.66 (s, 2 H, CH_2Si), 3.59 (d, J = 15.1 Hz, 1 H, CHPh), 3.82 (s, 3 H, OCH_3), 4.61 (s, 2 H, NCH-CH=), 5.25 (d, J = 15.1 Hz, 1 H, CHPh), 6.8-7.4 (m, 9 H, Ph and C_6H_4OMe). ^{13}C NMR (50 MHz), -3.6 ($SiCH_3$), -3.5 ($SiCH_3$), 18.5 (2 × CH_3), 20.1 (CH_2Si), 20.7 (2 × CH_3), 23.5 (SiC), 34.6 ($CHMe_2$), 48.6 (NCH_2), 55.3 (OCH_3), 57.8 (C-4), 98.0 (C-5), 114.3, 127.6, 128.1, 128.3, 128.6, 132.8, 136.0, 149.0 (C-6), 151.0 (C-2), 159.6.

Methyl *N*-(4-methoxyphenyl)-*N*-[4-(dimethyl(1,1,2-trimethylpropyl)silyl)-3-oxobutyl]carbamate (51). According to the procedure used for **33** and **34**, methoxymethyl compound **22** (171 mg, 0.759 mmol) was treated with **49** (413 mg, 2.26 mmol) and a 1.0 M solution of $TiCl_4$ (0.9 mL, 0.90 mmol) in 5 mL of CH_2Cl_2 to give **51** (84.9 mg, 2.16 mmol, 28%) as a light brown oil. R_f 0.65 (EtOAc/hexane: 1/4). ^{1}H NMR (200 MHz) 0.07 (s, 6 H, $Si(CH_3)_2$), 0.83 (s, 6 H, $C(CH_3)_2$), 0.86 (d, J = 6.9 Hz, 6 H, $CH(CH_3)_2$), 1.61 (septet, 1 H, $CH(CH_3)_2$), 2.23 (s, 2 H, CH_2Si), 2.65 (t, J = 6.1 Hz, 2 H, CH_2C=O), 3.33 (t, J = 6.1 Hz, 2 H, CH_2N), 3.65 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 6.57 (d, J = 8.1 Hz, 2 H), 6.76 (d, J = 8.1 Hz, 2 H). ^{13}C NMR (50 MHz) 2.4 ($Si(CH_3)_2$), 18.5 ($(CH_3)_2$), 20.5 ($(CH_3)_2$), 23.6 (SiC), 34.4 ($CHMe_2$), 35.5 (CH_2Si), 39.8, 43.4, 55.3 (OCH_3), 55.8 (OCH_3), 114.6, 114.9, 141.9 (C-1), 152.3 (C-4), 156.1 (NC=O), 209.3 (C=O). Accurate mass 393.2331 (calcd for $C_{21}H_{35}NO_4Si$ 393.2336).

Ethyl *N*-benzyl-*N*-[1-(4-methoxyphenyl)-3-butenyl]carbamate (53). According to procedure B, carbamate **14** (154 mg, 0.447 mmol) was treated with allyltrimethylsilane (0.25 mL, 1.6 mmol) and $EtAlCl_2$ (1.8 M in toluene, 0.30 mL, 0.54 mmol) to give **53** (150 mg, 0.434 mmol, 97%) as a light-pink oil. R_f 0.55 (EtOAc/hexane: 1/4). IR 2840 (OMe), 1680 (NC=O). ^{1}H NMR (100 MHz) 1.20 (t, J = 7 Hz, 3 H, OCH_2CH_3), 2.62 (m, 2 H, CH_2-CH=), 3.76 (s, 3 H, OCH_3), 4.08 (d, J = 16 Hz, 1 H, CHPh), 4.17 (q, J = 7 Hz, 2 H, OCH_2CH_3), 4.40 (d, J = 16 Hz, 1 H, CHPh), 4.85-5.10 (m, 2 H, $=CH_2$), 5.34 (t(b), J = 8 Hz, 1 H, NCH), 5.45-5.95(m, 1 H, -CH=), 6.75-7.35 (m, 9 H, Ph and C_6H_4OMe). ^{13}C NMR (63 MHz) 14.5 (CH_3), 36.0 (CH_2CH=), 47.3 (NCH_2), 55.0 (OCH_3), 58.7 (NCH), 61.2 (OCH_2), 113.6, 116.9 ($=CH_2$), 126.5, 127.4, 127.9, 129.3, 131.5, 134.9, 139.1 (-CH=), 156.8 (NC=O), 158.9. Accurate mass 339.1839 (calcd for $C_{21}H_{25}NO_3$ 339.1834).

Ethyl *N*-benzyl-*N*-[1-(2-furyl)-3-butenyl]carbamate (54). According to procedure B, carbamate **19** (200 mg, 0.659 mmol) was treated with allyltrimethylsilane (0.30 mL, 1.89 mmol), and $EtAlCl_2$ (1.8 M in toluene, 0.44 mL, 0.79 mmol) to give **54** (89 mg, 0.30 mmol, 46%) as a colourless oil. R_f 0.55 (EtOAc/hexane: 1/4). IR 1680 (NC=O). ^{1}H NMR (100 MHz) 1.19 (bt, J = 7 Hz, 3 H, OCH_2CH_3), 2.56 (m, 2 H, -CH_2CH=), 4.17 (d, J = 15 Hz, 1 H, CHPh), 4.16 (q, J = 7 Hz, 2 H, OCH_2), 4.44 (d, J = 15 Hz, 1 H, CHPh), 4.85-5.10 (m, 2 H, $=CH_2$), 5.25-5.95 (m, 2 H, -CH= and NCH), 6.21 (m, 2 H, furfuryl H^3 and H^4), 6.95-7.35 (m, 6 H, Ph, and furfuryl H^5). ^{13}C NMR (63 MHz) 14.4 (CH_3), 35.4 (CH_2CH=), 47.0 (NCH_2), 53.4 (NCH), 61.4 (OCH_2), 108.3, 109.9, 117.5, 126.5, 127.1, 127.9 (2 × C), 134.0, 138.9, 152.9 (fufuryl C-2), 156.6 (NC=O). Accurate mass 299.1535 (calcd for $C_{18}H_{21}NO_3$ 299.1521).

3-Benzyl-4-(4-methoxyphenyl)-6-methylene-tetrahydro-1,3-oxazin-2-one (55). Formic acid (1 mL) was added to **23** (138 mg, 0.362 mmol) and stirred for 1.5 h at room temperature. The reaction mixture was poured into saturated aq $NaHCO_3$ and

extracted with chloroform (3 ×). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to give **55** (107 mg, 0.348 mmol, 96%) as a colourless oil. R_f 0.45 (EtOAc/hexane: 1/4). IR 2840 (OMe), 1710 (NC=O), 1665 (=-O). ^{1}H NMR (200 MHz) 2.43 (dd, J = 14.2, 2.8 Hz, 1 H), 2.80 (dd, J = 14.2, 6.2 Hz, 1 H), 3.65 (d, J = 15.1 Hz, 1 H, CHPh), 3.79 (s, 3 H, OCH_3), 4.05 (t, J = 1.5 Hz, 1 H, $=CH^E$), 4.33 (dd, J = 6.1 Hz, J = 2.8 Hz, 1 H, H^4), 4.70 (s, 1 H, $=CH^Z$), 5.25 (d, J = 15.1 Hz, 1 H, CHPh), 6.7-7.5 (m, 9 H, Ph and C_6H_4OMe). ^{13}C NMR (63 MHz) 34.4 (C-5), 50.3 (NCH_2), 55.2 (OCH_3), 55.5 (C-4), 94.8 ($=CH_2$), 114.2, 127.6, 127.8, 128.1, 128.7, 130.6, 136.3, 150.2, 151.5, 159.5. Accurate mass 309.1372 (calcd for $C_{19}H_{19}NO_3$ 309.1365).

3-Benzyl-4-phenyl-6-methylene-tetrahydro-1,3-oxazin-2-one (56). Formic acid (0.50 mL) was added to **24** (72.7 mg, 0.217 mmol) and stirred for 1 h at room temperature. The reaction mixture was poured into saturated aq $NaHCO_3$ and extracted with chloroform (3 ×). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to give **56** (54.7 mg, 0.196 mmol, 95%) as a colourless oil. IR 1710 (NC=O), 1665 (=-O). ^{1}H NMR (100 MHz) 2.48 (dd, J = 14, 3 Hz, 1 H), 2.85 (ddt, J = 14, 6, 1.5 Hz, 1 H), 3.66 (d, J = 15 Hz, 1 H, CHPh), 4.03 (t, J = 1.5 Hz, 1 H, $=CH^E$), 4.39 (dd, J = 6, 3 Hz, 1 H, H^4), 4.69 (s, 1 H, $=CH^Z$), 5.28 (d, J = 15 Hz, 1 H, CHPh), 7.0-7.5 (m, 10 H, 2 × Ph). ^{13}C NMR (63 MHz) 34.2 (C-5), 50.5 (NCH_2), 56.0 (C-4), 94.9 ($=CH_2$), 126.3, 127.8, 128.1, 128.3, 128.7, 128.8, 136.2, 138.6, 150.0, 151.4. Accurate mass 279.1263 (calcd for $C_{18}H_{17}NO_2$ 279.1259).

Reaction of oxazinone 23 with cesium fluoride in acetonitrile. Under a dry nitrogen atmosphere, CsF (296 mg, 1.35 mmol) was added to a solution of **23** (96 mg, 0.25 mmol) in 4 mL of CH_3CN. The reaction mixture was stirred for 3 h at room temperature and then poured into brine. The aqueous layer was extracted with chloroform (4 ×). The combined extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed to yield an 20:80 mixture of **55** and **3-benzyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydro-2*H*-1,3-oxazin-2-one (57)** (65 mg, 0.21 mmol, 84%) and as a colourless oil. R_f 0.45 (EtOAc/hexane: 1/4). ^{1}H NMR (100 MHz) **57**: 1.87 (d, J = 1 Hz, 3 H, $=CCH_3$), 3.69 (d, J = 15 Hz, 1 H, CHPh), 4.60 (m, 1 H), 4.78 (m, 1 H), 5.22 (d, J = 15 Hz, 1 H, CHPh), 6.8-7.4 (m, 9 H, Ph and C_6H_4OMe). ^{13}C NMR (63 MHz) **57**: 18.2 (CH_3), 48.5 (NCH_2), 55.3 (OCH_3), 57.9 (C-4), 100.4 (C-6), 114.4, 127.7, 128.2, 128.4, 128.6, 132.1, 135.7, 146.1 (C-6), 150.9 (C-2), 159.7.

***rel*-(4*R*,5*R*)-3-Benzyl-5-bromo-4-(4-methoxyphenyl)-6-methylene-tetrahydro-1,3-oxazin-2-one (59).** Under a dry nitrogen atmosphere, a solution of Br_2 (88 mg, 0.55 mmol) in 6 mL of CCl_4 was added dropwise to a solution of **23** (207 mg, 0.542 mmol) in 5 mL of CCl_4 at -20 °C. The reaction mixture was stirred for 0.25 h at -20 °C, then warmed up to room temperature and after 2 h stirring concentrated *in vacuo*. The residue was chromatographed to give **59** (154 mg, 0.399 mmol, 73%) as a colourless crystalline solid, mp 130-131 °C (benzene). R_f 0.25 (EtOAc/hexane: 1/4). IR 2840 (OMe), 1725 (CO), 1655 (=-O). ^{1}H NMR (100 MHz) 3.71 (d, J = 14 Hz, 1 H, CHPh), 3.80 (s, 3 H, OCH_3), 4.31 (d, J = 2 Hz, 1 H, $=CH^E$), 4.47 (d, J = 1.5 Hz, 1 H), 4.53 (d, J = 1.5 Hz, 1 H), 4.78 (d, J = 2 Hz, 1 H, $=CH^Z$), 5.27 (d, J = 14 Hz, 1 H, CHPh), 6.75-7.40 (m, 9 H, Ph and C_6H_4OMe). ^{13}C NMR (63 MHz) 43.6 (C-5), 50.9 (NCH_2), 55.2 (OCH_3), 63.7 (C-4), 97.2 ($=CH_2$), 114.5, 127.6, 127.9, 128.3, 128.4, 128.9, 134.8, 149.4, 149.5, 160.1. Accurate mass 387.0462 (calcd for $C_{19}H_{18}NO_3{}^{79}Br$ 387.0470). Crystallographic data: Orthorhombic, $P2_12_12_1$, a 11.4186(7) Å, b 31.532(2) Å, c 9.9865(5) Å, V = 3595.6(4) Å^3, Z = 8, D_x = 1.43 gcm^{-3}, λ(CuKα) = 1.5418 Å, μ(CuKα) = 32.56 cm^{-1}, F(000) = 1584, room temperature, Final R = 0.043 for 2857 observed reflections. Lists of refined coordinates and e.s.d.'s, bond distances and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

***rel*-(4*R*,5*S*)-5-Aminocarbonyl-3-benzyl-6-methylene-4-phenyl-tetrahydro-1,3-oxazin-2-one (61).** Under a dry nitrogen atmosphere, chlorosulfonyl isocyanate (92 µL, 1.1 mmol) was added to a solution of **24** (201 mg, 0.646 mmol) in 2 mL of CCl_4 at 0 °C. After 15 min, the reaction mixture was allowed to warm to room temperature and stirred for 18 h. The reaction mixture was concentrated *in vacuo*. A mixture of 6 mL of acetone, 2.5 mL of water and 1 mL 3 M HCl was added to the residue after being stirred for 3 h. The mixture was poured into water and extracted with CH_2Cl_2 (5 ×). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed to give **61** (127 mg, 0.394 mmol, 61%) as a white solid, mp 170-171 °C. R_f 0.60 (EtOAc). IR 3510 and 3400 (NH_2), 1720 (NC=O), 1700 (C=ONH_2), 1660 (=-O). ^{1}H NMR (100 MHz) 3.27 (d, J = 1.5 Hz, 1 H, *CH*CONH_2), 3.88 (d, J = 15 Hz, 1 H, CHPh), 4.27 (d, J = 2 Hz, 1 H, $=CH^E$), 4.92 (d, J = 2 Hz, 1 H, $=CH^Z$), 4.99 (d, J = 15 Hz, 1 H, CHPh), 5.05 (s, 1 H, H^4), 6.30 (bs, 2 H, NH_2), 7.2 (m, 10 H, 2 × Ph). ^{13}C NMR (50 MHz) 51.3 (C-5), 51.8 (NCH_2), 58.4 (C-4), 99.0 ($=CH_2$), 126.2, 127.9, 128.4, 128.4, 128.7, 129.0, 135.3, 138.0, 149.2, 150.3, 168.4 (C=ONH_2). Accurate mass 322.1321 (calcd for $C_{19}H_{18}N_2O_3$ 322.1318).

***rel*-(4*R*,5*S*)-5-Acetyl-3-benzyl-4-(4-methoxyphenyl)-6-methylene-tetrahydro-1,3-oxazin-2-one (62).** Under a dry nitrogen atmosphere, fresh distilled AcCl (0.17 mL, 2.4 mmol) was added to a suspension of $AlCl_3$ (0.30 g, 2.3 mmol) in 6 mL of CH_2Cl_2 at 0 °C, and stirred for 1 h. This solution was added dropwise to a solution of **23** (572 mg, 1.50 mmol) in 5 mL of CH_2Cl_2 at -78 °C. After stirring for 0.75 h at -78 °C, the reaction mixture was warmed up to room temperature and stirred for 1 h. The reaction mixture was poured out into a mixture of ice and saturated aq $NaHCO_3$. After extraction of the aq layer with chloroform (4 ×), the combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo*. The residue was chromatographed to give **62** (308 mg, 0.876 mmol, 58%) as a light-yellow oil. R_f 0.20 (EtOAc/hexane: 1/4). IR 2840 (OMe), 1720 (MeC=O and NC=O), 1660 (=-O). ^{1}H NMR (100 MHz) 2.25 (s, 3 H, $COCH_3$), 3.27 (d, J = 1.5 Hz, 1 H, H^5), 3.76 (d, J = 15 Hz, 1 H, CHPh), 3.78 (s, 3 H, OCH_3), 4.31 (d, J = 2 Hz, 1 H, $=CH^E$), 4.76 (d, J = 1.5 Hz, 1 H, H^4), 4.95 (d, J = 2 Hz, 1 H, $=CH^Z$), 5.05 (d, J = 15 Hz, 1 H, CHPh),

6.75-7.40 (m, 9 H, Ph and C_6H_4OMe). ^{13}C NMR (63 MHz) 27.2 (CH_3), 50.9 (NCH_2), 55.1 (OCH_3), 56.2, 57.3, 98.8 (=CH_2), 114.2, 127.4, 127.7, 128.2, 128.7, 129.8, 135.2, 148.5, 150.2, 159.5, 194.8 (C=OCH_3). Accurate mass 351.1470 (calcd for $C_{21}H_{21}NO_4$ 351.1471).

5-Acetyl-3-benzyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydro-2*H*-oxazin-2-one (63). Under a dry nitrogen atmosphere, Et_3N (50 μL, 0.35 mmol) was added to a solution of **62** (79 mg, 0.22 mmol) in 1 mL of CH_2Cl_2 and stirred for 2.5 days. The reaction mixture was concentrated *in vacuo* and the residue was chromatographed to give **63** (75 mg, 0.21 mmol, 96%) as a light-yellow oil. R_f 0.60 (EtOAc/hexane: 1/1). IR 2840 (OMe), 1720 (MeC=O and NC=O), 1650 (=-O). ^1H NMR (200 MHz) 2.04 (s, 3 H, =C-CH_3), 2.35 (s, 3 H, $COCH_3$), 3.69 (d, J = 15 Hz, 1 H, CHPh), 3.75 (s, 3 H, OCH_3), 4.96 (s, 1 H, H^4), 5.10 (d, J = 15 Hz, 1 H, CHPh), 6.84 (d, J = 8 Hz, 2 H), 7.14 (d, J = 8 Hz, 2 H), 7.2-7.5 (m, 5 H, Ph). ^{13}C NMR (50 MHz) 19.2 (CH_3), 30.5 (C=OCH_3), 48.8 (NCH_2), 55.2 (OCH_3), 57.5 (C-4), 114.4, 116.0 (C-5), 128.0, 128.1, 128.8, 128.9, 130.7, 135.1, 149.5 (C-2), 157.5 (C-6), 159.8, 195.0 (*C*=OCH_3). Accurate mass 351.1456 (calcd for $C_{21}H_{21}NO_4$ 351.1471).

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