Intramolecular Iron(II)-catalyzed Nitrogen Transfer Reactions of Unsaturated Alkoxycarbonyl Azides: A Facile and Stereoselective Route to 4,5-Disubstituted Oxazolidinones

Thorsten Bach,* Björn Schlummer, and Klaus Harms[a]+

Dedicated to Professor David A. Evans on the occasion of his 60th birthday

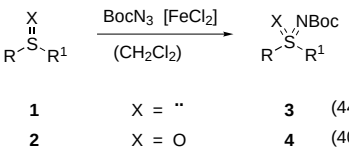
Abstract: Intramolecular Fe^{II}-catalyzed reactions of various unsaturated alkoxycarbonyl azides are described. The reactions occur in the presence of stoichiometric amounts of trimethyl silyl chloride employing ethanol as the solvent. The corresponding 2-alkenyloxycarbonyl azides **5**, **9**, **18**, **20**, **22**, and **24** gave the products **7**/**8**, **10**/**11**, **19**, **21**, **23**, and **25** of an olefin chloroamination in moderate to good yields (47 – 72 %). The facial diastereoselectivity of the ring closing C–N-bond forming step is good both in cyclic (**20**, **24**) and in acyclic substrates (**5**, **18**, **22**) (> 90 % *ds*). The subsequent chlorine atom transfer occurs selectively in cyclic systems (**20**, **24**) and in systems (**9b**, **18**) which exhibit a conformational bias in the postulated radical intermediate **14**. The lifetime τ of this elusive intermediate was estimated from the loss of stereochemical information in conformationally unrestricted systems (**9a**, **22**) and from the data obtained with a radical clock (**31** → **32**). 2-Alkynyloxycarbonyl azides **34** and **36** also yield chloroamination products which are obtained exclusively as the (*Z*)-isomers **35** and **37** (81 – 99 % yield). The products of the *tert*-butyl-substituted substrates **38** undergo an immediate rearrangement/solvolysis reaction in the reaction mixture and gave the 5-alkoxyoxazolidinones **39** (93 – 99 % yield).

Keywords: cyclization · homogeneous catalysis · iron · nitrogen heterocycles · radical reactions

Introduction

The reaction of alkoxycarbonyl azides and alkenes is known to yield 1-alkoxycarbonyl-1,2,3-triazolines.[1] Strained alkenes and alkenes activated by electron-releasing groups react readily whereas the reaction of non-activated olefins is slow.[2, 3] The corresponding triazolines can be converted into aziridines through nitrogen extrusion.[3] Alternatively, aziridines are directly accessible by thermal or photochemical decomposition of alkoxycarbonyl azides in the presence of alkenes.[4, 5] Transition metal catalyzed processes of the latter type have to the best of our knowledge not been studied.[6]

We have recently shown that *tert*-butyloxycarbonyl azide ($BocN_3$) is a suitable precursor for the generation of a *N*-Boc-protected nitrogen fragment "BocN" by transition metal catalysis.[7] In the presence of $FeCl_2$ a rapid nitrogen evolution occurs and the amide $BocNH_2$ is obtained as the major product after work-up. If sulfur nucleophiles are employed as reaction partners, $BocN_3$ allows for a smooth $FeCl_2$-catalyzed imidation (Scheme 1). Thus, sulfimides **3** and sulfoximides **4** are available from sulfides **1** and from sulfoxides **2**. Subsequent 2,3-rearrangement reactions of allyl sulfimides yield *N*,*N*-diprotected allyl amines in good yields.[7c]



Scheme 1. The Fe^{II}-catalyzed imidation of sulfides **1** and sulfoxides **2** with $BocN_3$.

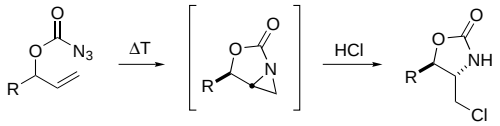
The intermolecular Fe^{II}-catalyzed reaction of $BocN_3$ with alkenes proceeded sluggishly. Only electron rich alkenes gave a notable conversion.[7a] With silyl enol ethers and ketene acetals the 1,3-dipolar cycloaddition/dediazotation was a significant background reaction[3c,e] which made it difficult to distinguish between the catalyzed and the uncatalyzed pathway.[8] In view of these problems we looked into the possibility of an intramolecular nitrene transfer which was expected to occur in unsaturated azidoformates. Recent studies by

[a] Prof. Dr. T. Bach,[+] Dipl.-Chem. B. Schlummer, Dr. K. Harms+
Fachbereich Chemie der Philipps-Universität
Hans-Meerwein-Strasse, 35032 Marburg (Germany)
E-mail: thorsten.bach@ch.tum.de

[+] New address:
Lehrstuhl für Organische Chemie I, Technische Universität München
Lichtenbergstrasse 4, 85747 Garching (Germany)
Fax: (+49) 89-289-13315

[+] Crystal structure determination

Bergmeier et al. revealed that a thermal decomposition of alkenyl azidoformates (alkenyloxycarbonyl azides) yields bicyclic aziridines which in turn undergo a facile ring opening to substituted oxazolidinones.[5] This intriguing reaction sequence is exemplified by the reaction of azide **5a** which upon heating in 1,1,2,2-tetrachloroethane (TCE) yielded the 5-chloromethyl substituted oxazolidinone **7a** via aziridine **6a** as intermediate (Scheme 2). The ring opening was caused by hydrochloric acid which is likely to be formed from the solvent at elevated temperature.



5a **6a** **7a**

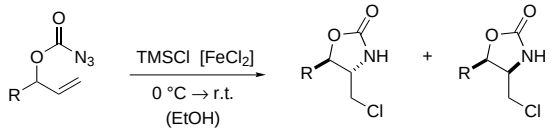
Scheme 2. Thermal intramolecular aziridination and ring opening of the 2-propenyloxycarbonyl azide **5a**.

At room temperature there is no intramolecular reaction of alkenyl azidoformates. It consequently appealed to us to study possible Fe^{II}-catalyzed reactions of these substrates more closely. We initially considered an aziridination via nitrene transfer as the most likely reaction to occur.[8] The possibility of an enantioselective aziridination,[9, 10] for example by ligand tuning at the metal center, was a major benefit we associated with a catalyzed versus a thermally induced pathway. In order to investigate the general applicability of the planned reaction we tested several substrates and looked more closely into the mechanism. The results of this study are summarized in the following account.[11] As it turned out the Fe^{II}-catalyzed decomposition of unsaturated azido formates does *not* follow an aziridination pathway. On the contrary, the reaction has to be envisaged as an intramolecular chloroamination initiated by an electron-deficient intermediate. This new intramolecular reaction pathway accessible to azides and alkenes in the presence of $FeCl_2$ has been further investigated by structural and spectroscopic studies. The unexpected mechanistic course has an additional impact on the scope of the reaction. It is applicable not only to alkenyl azidoformates but also to the corresponding alkynyl derivatives.[11b]

Abstract in German: *Intramolekulare Fe^{II}-katalysierte Reaktionen verschiedener ungesättigter Alkoxycarbonylazide werden beschrieben. Die Umsetzungen vollziehen sich in Gegenwart stöchiometrischer Mengen von Trimethylsilylchlorid in Ethanol als Lösungsmittel. Die entsprechenden 2-Alkenyloxycarbonylazide **5**, **9**, **18**, **20**, **22** und **24** ergaben die Produkte **7/8**, **10/11**, **19**, **21**, **23** und **25** einer olefinischen Chloraminierung in mittelmäßigen bis guten Ausbeuten (47–72 %). Die faciale Diastereoselektivität der ringschließenden C–N-Bindungsbildung ist sowohl in cyclischen (**20**, **24**) als auch in acyclischen (**5**, **18**, **22**) Substraten gut (>90 % ds). Der nachfolgende Chloratom-Transfer verläuft in cyclischen Systemen (**20**, **24**) und in Systemen, in denen die freie Rotation in einem postulierten Radikalintermediat **14** eingeschränkt ist (**9b**, **18**), mit hoher Selektivität. Die Lebensdauer τ dieses Intermediats wurde aus dem Verlust der stereochemischen Information in konformationell ungehinderten Systemen (**9a**, **22**) und aus den Daten, die mit einer Radikaluhr (**31** → **32**) erhalten wurden, abgeschätzt. 2-Alkinyloxycarbonylazide **34** und **36** lieferten ebenfalls Chloraminierungsprodukte, die ausschließlich als (Z)-Isomere **35** und **37** anfielen (81–99 % Ausbeute). Die Produkte der tert-Butyl-substituierten Substrate **38** unterzogen sich unter den Reaktionsbedingungen einer Umlagerung/Solvolyse und ergaben die 5-Alkoxyoxazolidinone **39** (93–99 % Ausbeute).*

Results and Discussion

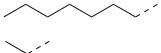
Reaction of alkenyloxycarbonyl azides: In preliminary experiments, we found that $FeCl_2$ was suited to promote the intramolecular reaction of 2-alkenyloxycarbonyl azides, such as compound **5a**. Not unexpectedly, the apparent ring opening product **7a** was formed in which a chlorine atom is incorporated. If $FeCl_2$ was to deliver the chlorine atom it had to be used stoichiometrically. The reaction of compound **5a** with $FeCl_2$ (0.5 equiv) in acetonitrile as the solvent yielded 59 % of the desired product **7a**. We quickly discovered that TMSCl can be employed as a stoichiometric chlorine source. This finding enabled us to use $FeCl_2$ in catalytic quantities and paved the way to the Fe^{II}-catalyzed aminochlorination depicted in Scheme 3. Several substrates were employed in the reaction to give acceptable yields (Scheme 3, Table 1). In general, more complex, less volatile substrates gave better yields than substrates with similar substitution pattern but



5 **7** **8**

Scheme 3. Fe^{II}-catalyzed intramolecular chloroamination of the 2-propenyloxycarbonyl azides **5**.

Table 1. Preparation of the 4,5 disubstituted oxazolidinones **7** and **8** according to Scheme 3.

	Azide	R	$FeCl_2$ [mol %]	Products	Yield[a] [%]	*d.r.*[b] [**7**/**8**]
1	**5a**		10	**7a/8a**	72	91/9
2	**5b**		10	**7b/8b**	64	88/12
3	**5c**		30	**7c/8c**[c]	60	94/6
4	**5d**		10	**7d/8d**	60	88/12
5	**5e**		30	**7e/8e**	33	92/8
6	**5f**		10	**7f/8f**	68	90/10

[a] Yield of isolated product. [b] The diastereomeric ratio was determined by integration of appropriate ^1H NMR signals. [c] Mixture of two 4,5-*trans*-isomers due to the additional stereogenic center at the cyclohexene ring.

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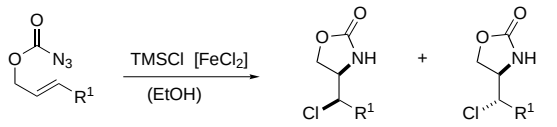
lower molecular weight, for example entry 1 versus entry 5. The facial diastereoselectivity, as expressed by the ratio of *trans*- (**7**) and *cis*-diastereoisomer (**8**) was in direction and size equal to the selectivity recorded for the thermal reaction.[5a] The direction of the face discrimination can be interpreted by conventional 1,3-allylic strain arguments which are valid for an electrophilic attack at a double bond adjacent to a stereogenic center.[12]

The starting materials **5** were conveniently prepared from the corresponding allylic alcohols according to a known procedure.[13] Successive treatment of the alcohols with 1,1′-carbonyldiimidazole (CDI)/pyridine in benzene and subsequent reaction with NaN_3 in DMF gave the desired azides in good to excellent yields.

The results depicted in Scheme 3 and Table 1 were anticipated based on the expected analogy of thermal and metal-catalyzed reactions. The azidoformates **9** derived from (*E*)-configured allylic alcohols, however, showed significant deviations in the stereochemical outcome of the chloroamination (Scheme 4). The thermal reactions proceeded stereo-

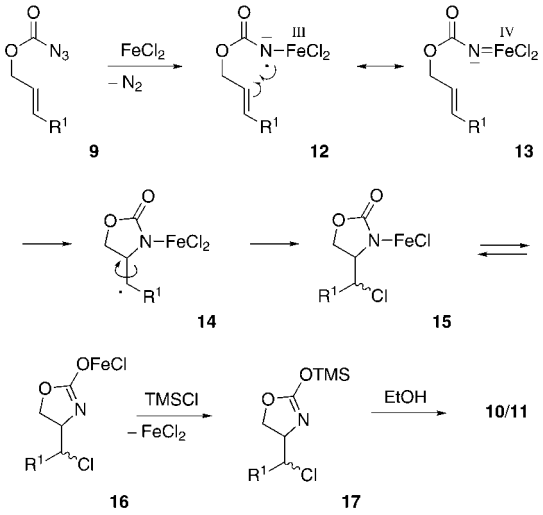


9a	R^1 = *n* Pr	(84%)	**10a**	49/51	**11a**
9b	R^1 = Ph	(76%)	**10b**	>99/1	**11b**

Scheme 4. Fe^{II}-catalyzed chloroamination of the 2-alkenyloxycarbonyl azides **9**.

specifically through a *syn*-aziridination and a subsequent S_N2-type ring opening. The *erythro*-products **11** were the only detectable oxazolidinones which could be obtained from compounds **9** upon heating in TCE (**11a**: 62%, **11b**: 42%).[11a] Contrary, the Fe^{II}-catalyzed reactions yielded exclusively the *threo*-product **10b** if azide **9b** was employed and a mixture of *threo*- and *erythro*-products **10a** and **11a** if the *n*-propyl substituted azide **9a** was the substrate. The relative configuration of product **10b** was proven by single crystal X-ray analysis.[11a]

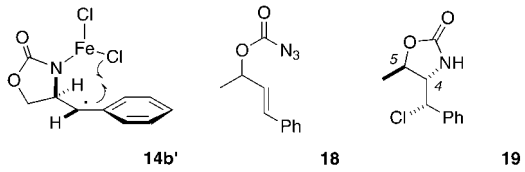
An (*E*)/(*Z*)-isomerization or a subsequent equilibration of the products **11** under the reaction conditions of the Fe^{II}-catalyzed process were ruled out by control experiments. Clearly, the reaction of azide **9a** is not stereospecific and an intermediate must be formed which allows for free rotation around the former C=C-bond. Bearing in mind that the nitrogen evolution is induced by $FeCl_2$ we suggest an electron transfer from Fe^{II} to the carbonyl group as the initial step of the reaction sequence[14] (Scheme 5); this in turn would lead to an α-cleavage of the N–N_2-bond and to the evolution of N_2. The resulting species can be formulated as a radical-like Fe^{III}-compound **12** or as an Fe^{IV}-nitrene complex **13**. While the latter description would explain a direct aziridination via nitrene transfer the former is apparently better suited to account for the reactivity pattern of this iron complex. Indeed, the intermediate **14** formed by radical addition to the olefinic double bond is a reasonable intermediate to explain the non-



Scheme 5. Proposed reaction course of the Fe^{II}-catalyzed intramolecular chloroamination.

stereospecific nature of the chloroamination. Subsequent chlorine atom transfer which is likely to occur in an intramolecular fashion yields the Fe^{II}-species **15**. There is no hint as to where the iron atom resides. Structure **16** is equal to **15** and possibly an even more relevant structure. $FeCl_2$ is liberated either by reaction with TMSCl to intermediate **17** or by direct HCl-mediated cleavage to the oxazolidinone diastereoisomers **10** and **11**.

According to this mechanistic picture the stereochemical result recorded for the chloroamination of compound **9a** is rationalized by an unrestricted rotation in intermediate **14a**. The high *threo*-selectivity with which the phenyl-substituted azide **9b** reacts is due to the restricted rotation around the C–C-single bond. There should be a clear preference for conformation **14b′** from which the chlorine transfer can occur



intramolecularly. A *threo*-preference was also found in the reaction of the chiral azide **18** which yielded predominantly the 4,5-*trans*-substituted oxazolidinone **19** with a *threo*-relationship between the exocyclic stereogenic center and the stereogenic center at C4. The crystal structure of this compound is depicted in Figure 1.[15]

Further evidence for an intramolecular chlorine atom transfer in intermediates related to **14** was collected from the study of a cyclic alkenyloxycarbonyl azide. The 1-cyclo-2-hexenol-derived azide **20** gave exclusively the bicyclic product **21** (Scheme 6) the relative configuration of which was proven by single crystal X-ray analysis (Figure 2).[16] After formation of the five-membered oxazolidinone ring the chlorine atom is apparently delivered from the same face to which the $FeCl_2$ fragment is coordinated via the nitrogen or the oxygen atom.

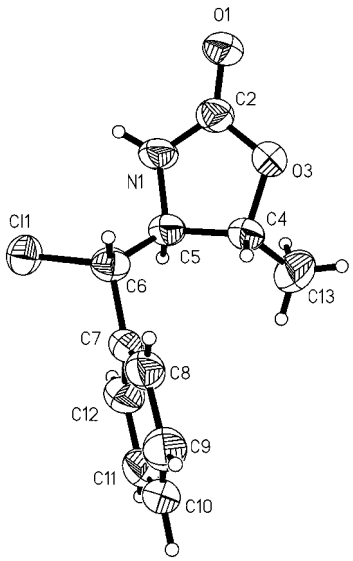
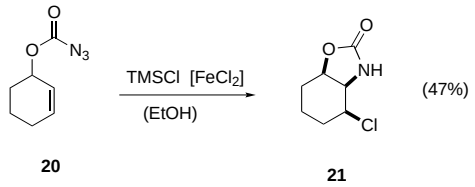


Figure 1. A molecule of compound **19** in the crystal.



Scheme 6. Fe^{II}-catalyzed chloroamination of 3-azidocarbonyloxy-1-cyclohexene (**20**).

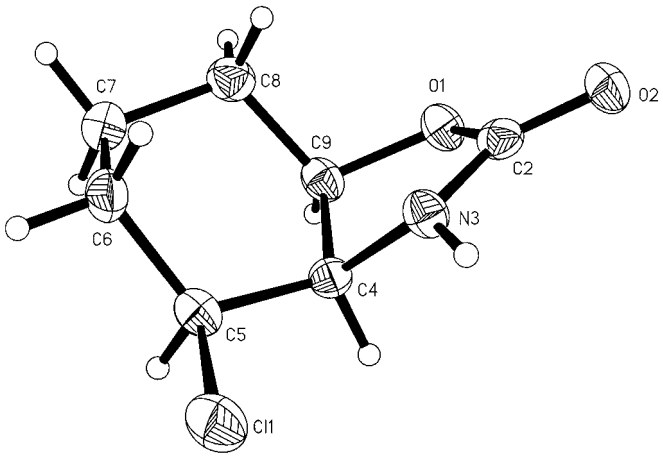
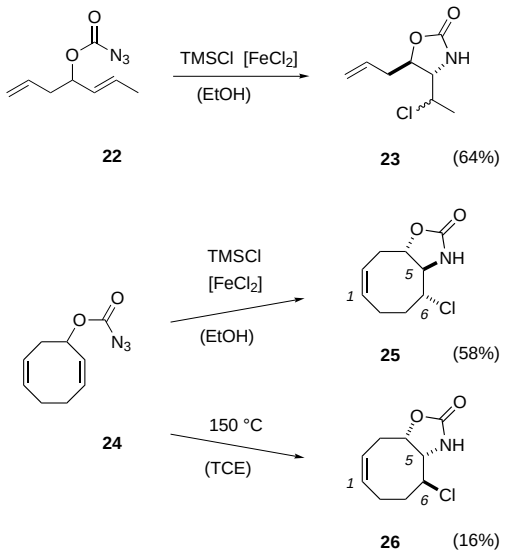


Figure 2. A molecule of compound **21** in the crystal.

Radical clocks: The loss of stereochemical information in the reaction of the (*E*)-configured azide **9a** allows to calculate an upper value for the rate of chlorine transfer in the postulated intermediate **14**. It is estimated at $k_{max} \leq 5.7 \times 10^{11}\ s^{-1}$ assuming a rotational barrier of $\geq 15\ kJ\,mol^{-1}$ at 300 K. Radical clocks were considered as suitable tools to obtain further kinetic data on intermediate radicals such as **14**. Initial studies were driven by our synthetic interests and by the relevant comparison of the Fe^{II}-catalyzed reaction and the thermal reaction. Substrate **5f** was in principle already suited for a second 5-*exo*-trig ring closure which was not observed. Similarly, substrate **22** yielded only the oxazolidinone **23** and no bicyclic products (Scheme 7). The Fe^{II}-catalyzed decomposition of azide **24** gave no hint on the formation of a conceivable diquinane. The sole product isolated was the oxazolidinone **25** which structure was elucidated by single crystal X-ray analysis (Figure 3).[17]



Scheme 7. Fe^{II}-catalyzed chloroamination of 4-azidocarbonyloxy-1,5-heptadiene (**22**) and 3-azidocarbonyloxy-1,5-cyclooctadiene (**24**).

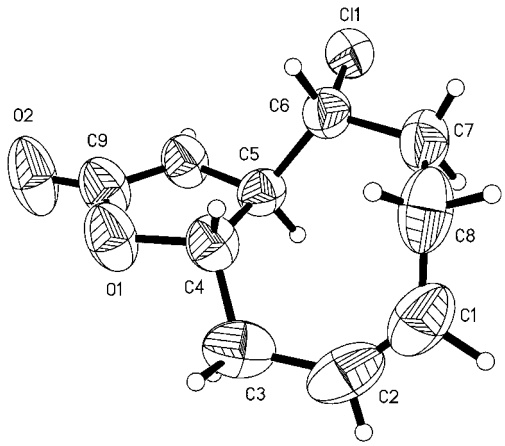


Figure 3. A molecule of compound **25** in the crystal.

The structure of product **25** deserves some comment. It is apparent from the X-ray analysis that the *trans*-oxazolidinone is fully planar and not significantly strained. Moreover, the intermediate radical formed by nitrogen attack at the double bond can abstract the chlorine atom intramolecularly only such that an all-*trans*-arrangement at the eight-membered ring arises. In this respect, the result is fully in line with the mechanistic proposal detailed above although the *trans*-configuration of C5 and C6 of cyclooctene **25** seems to contradict an intramolecular chlorine atom transfer at first sight. The thermal reaction of compound **24** delivered a single product **26** in low yield (Scheme 7). Again, the proof of relative configuration was carried out by single crystal X-ray analysis (Figure 4).[18] The oxazolidinone is *cis*-configured whereas the relative configuration of C5 and C6 is *trans*.

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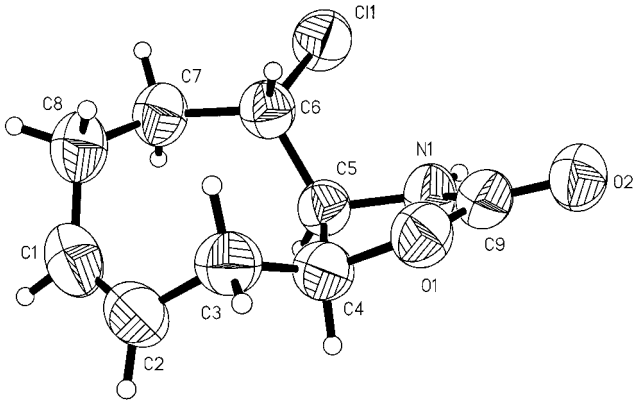
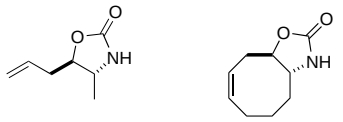


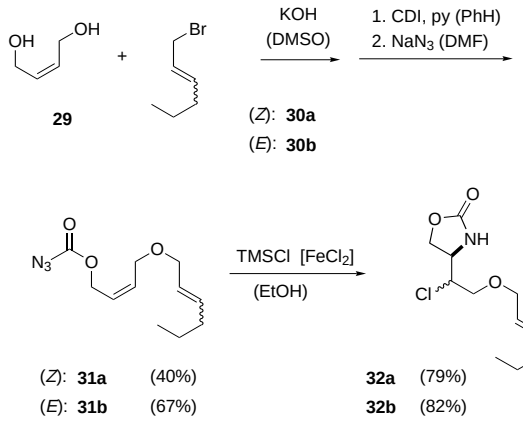
Figure 4. A molecule of compound **26** in the crystal.

As it was alluded to above, the substrates **5f**, **22**, and **24** were more or less used accidentally as radical clocks and were actually prepared in another context. The fact that the radical center and the olefinic double bond, which is targeted for a second ring closure, are connected via an oxazolidinone puts steric constraints on the 1-hexenyl radical[19] which may slow down the expected cyclization. Control experiments revealed that the cyclization is slow even on the time scale of the Bu_3SnH reduction. Upon treatment of compounds **7f** and **25** with Bu_3SnH and AIBN as the initatior in benzene as the solvent the hydro-de-chlorinated products **27** and **28** were obtained (72% yield).



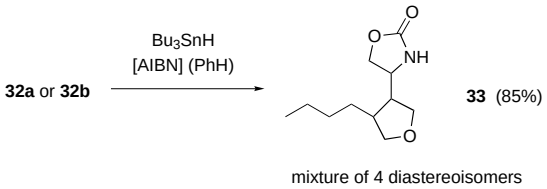
27 **28**

For the construction of conformationally unrestricted radical clocks we decided to place a suitable substituent at the position R^1 in substrate **9** (Scheme 5). Subsequent ring opening or ring closure can occur independently and should not be influenced by the oxazolidinone. Unfortunately, all attempts to construct cyclopropyl-substituted alkenyloxycarbonyl azides of this type were unsuccessful. The cyclopropane ring was not stable to the conditions employed for the conversion of the allylic alcohol to the azide. The cyclization of the 3-oxa-5-hexenyl radical to the (3-tetrahydrofuryl)methyl radical was subsequently considered as an alternative radical clock. It is remarkably fast ($k = 8.5 \times 10^6\ s^{-1}$)[14] compared with the 5-hexenyl → cyclopentylmethyl radical ring closure ($k = 2.5 \times 10^5\ s^{-1}$) and only slightly slower than the cyclopropylmethyl → 3-butenyl radical ring opening ($k = 10^8\ s^{-1}$).[20] In order to detect a ring closure we planned to subject both the (*E*)- and (*Z*)-isomer of the target compound to the chloroamination. Even if the ring opening after cyclization was fast and the chlorine transfer occurred exclusively in the open-chain radical, the double bond geometry would still indicate an intermediate cyclization. The synthesis of the substrates commenced with the two allyl bromides **30a** and **30b** which can be obtained in diastereomerically pure form (Scheme 8).[21] The monoalkylation of (*Z*)-1,4-butenediol (**29**) with either bromide **30** yielded the corresponding allylic alcohols which were directly converted into the alkenyloxycarbonyl azides **31a** and **31b**.



Scheme 8. Preparation and Fe^{II}-catalyzed chloroamination of the 2-alkenyloxycarbonyl azides **31**.

The Fe^{II}-catalyzed chloroamination was conducted under standard conditions (10 mol% $FeCl_2$, 1.5 equiv TMSCl, EtOH, 0 °C → RT, 21 h) without any tetrahydrofuran ring closure. The relative configuration of the double bonds was fully retained in the products. (*Z*)-Alkene **31a** was converted to the (*Z*)-product **32a** and (*E*)-alkene **31b** gave the (*E*)-diastereoisomer **32b**. Not unexpectedly, no significant preference for neither the *erythro*- nor the *threo*-diastereoisomer was observed in either reaction. A ratio of 5:95 was estimated as the limit (NMR spectroscopy) for the detection of the (*E*)-alkene **32b** in the presence of the (*Z*)-alkene **32a**. Assuming a rate constant of $8.5 \times 10^6\ s^{-1}$ for the ring closure a competing process which does not produce any ring-closed product within the detection limit must occur with a rate constant of $k \geq 1.6 \times 10^8\ s^{-1}$. The ring closure occurred readily when compounds **32a** and **32b** were subjected to the radical-based Bu_3SnH-reduction as depicted in Scheme 9. A mixture of four



Scheme 9. Radical-induced cyclization of the oxazolidinones **32**.

diastereoisomers was obtained without a significant preference for either diastereoisomer. One diastereoisomer was crystalline and its structure could be determined by X-ray analysis (Figure 5).[22]

Although the mechanism depicted in Scheme 5 is in accord with all experimental facts there are certainly alternative reaction pathways. We were not able to undoubtedly prove the presence of the postulated radical intermediate **14**. The radical clock employed allowed an estimation of its lifetime but we could not devise a radical clock fast enough to compete

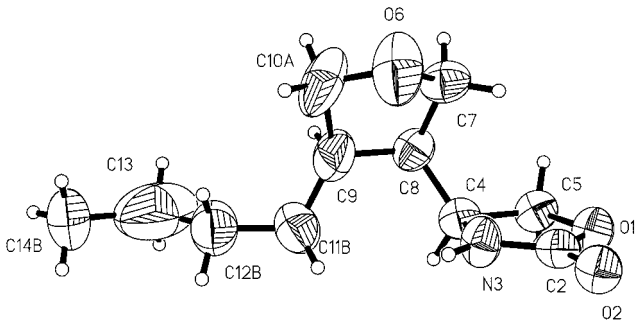
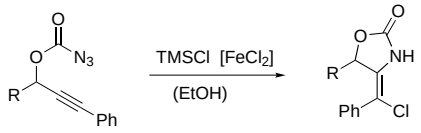


Figure 5. One diastereoisomer of compound **33** in the crystal.

with the postulated chlorine atom transfer. An important implication of the postulated mechanism was the fact that a chloroamination should also be possible for propargylic substrates. This extension is certainly not expected for an aziridination reaction nor for another reaction which proceeds via small ring intermediates.

Reaction of 2-alkynyloxycarbonyl azides: The formation of C–N-bonds by intra-[23] or intermolecular[24] attack of a nitrogen electrophile at a triple bond has been used less extensively than the corresponding reaction with alkenes. There are scattered reports on the activation of triple bonds by transition metals and subsequent nucleophilic nitrogen attack.[25] We initially studied the reaction of the phenyl-substituted 2-alkynyloxycarbonyl azides **34**. The substrates were readily available by alkynylation of aldehydes (RCHO) with litihium phenylacetylide and subsequent transformation of the propargylic alcohol to the azide via azidocarbonylation (CDI/py in benzene; NaN_3 in DMF).[13] A smooth reaction occurred upon treatment of the azides **34** with TMSCl and catalytic amounts of $FeCl_2$ in ethanol as the solvent (Scheme 10). The chloromethylidene-substituted oxazolidinones **35** were isolated in almost quantitative yields as crystalline, analytically pure solids (Table 2). In general, the use of 5 mol% of the catalyst was sufficient to guarantee high yields. A slight improvement was observed in some instances by raising the catalyst amount to 10 mol% (entries 3/4 and 5/6).



34 **35**

Scheme 10. Fe^{II}-catalyzed intramolecular chloroamination of the 2-propargyloxycarbonyl azides **34**.

The double bond in the products **35** is (*Z*)-configured as proven by NOE experiments and single crystal X-ray analysis. The crystal structure of compound **35d** is depicted in Figure 6.[26] It nicely illustrates the formal *cis*-chloroamination which according to our mechanistic picture occurs through nitrogen radical attack and subsequent chlorine transfer to the intermediate vinylic radical.

Table 2. Preparation of the (4-chloromethylidenyl)oxazolidinones (**35**) according to Scheme 10.

	Azide	R	$FeCl_2$ [mol%]	product	yield[a] [%]	(*Z*):(*E*)[b]
1	**34a**		5	**35a**	99	> 99/1
2	**34a**		10	**35a**	98	> 99/1
3	**34b**		5	**35b**	73	> 99/1
4	**34b**		10	**35b**	81	> 99/1
5	**34c**		5	**35c**[c]	79	> 99/1
6	**34c**		10	**35c**[c]	90	> 99/1
7	**34d**		10	**35d**	99	> 99/1
8	**34e**	H	10	**35e**	99	> 99/1

[a] Yield of isolated product. [b] (*Z*) and (*E*) refer to the double bond configuration. [c] Mixture of diastereoisomers due to the additional stereogenic center at the cyclohexene ring.

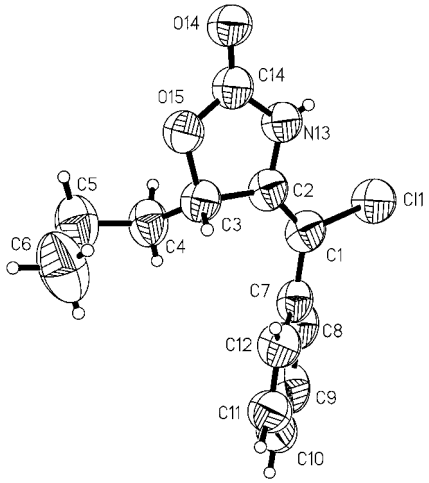
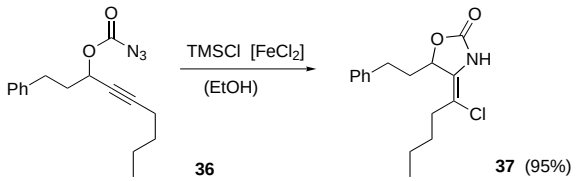


Figure 6. A molecule of compound **35d** in the crystal.

Although the oxazolidinones **35** proved to be stable in the solid state at room temperature they decomposed notably in solution. Distinct decomposition products could not be isolated. The tendency to decompose is even more pronounced in alkyl-substituted (4-chloromethylidene)oxazolidinones which were obtained as oils. As an example the synthesis of the *n*-butyl substituted product **37** from azide **36** is depicted in Scheme 11. Its constitution was proven by NMR spectroscopy whereas the relative configuration had to be



36 **37** (95%)

Scheme 11. Fe^{II}-catalyzed intramolecular chloroamination of the 2-propargyloxycarbonyl azide **36**.

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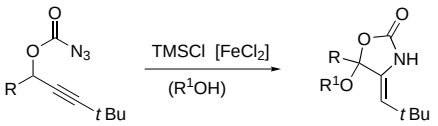
assigned based on analogy. The low stability of oxazolidinone **37** in $CDCl_3$ solutions precluded us from conducting more extensive NOE studies.

The structure of the products isolated from the chloroamination of *tert*-butyl substituted 2-alkynyloxycarbonyl azides **38** was suprising at first sight (Scheme 12). Instead of the *tert*-



Scheme 12. Fe^{II}-catalyzed cyclization of the 2-propargyloxycarbonyl azides **38**.

butylchloromethylidene fragment to be expected the oxazolidinones **39** carried a *tert*-butylmethylidene moiety at 4-position. There was no chlorine incorporation. The 5-position was, however, substituted by an additional alkoxy group which apparently stemmed from the solvent. The products were obtained in good yields. Some results are summarized in Table 3. As an additional solvent the chiral cyclopropyl methyl carbinol was used which yielded diastereomeric products due to an additional stereogenic center.[11b]

Table 3. Preparation of the (4-*tert*-butylmethylidenyl)oxazolidinones **39** according to Scheme 12.

	Azide	R	R^1	Product	Yield[a] [%]	(Z):(E)[b]
1	**38a**		Et	**39a**	93	>99/1
2	**38b**		Et	**39b**	95	>99/1
3	**38b**		*i*Pr	**39c**	99	>99/1

[a] The reaction was conducted with 10 mol% $FeCl_2$. Yield of isolated product. [b] (Z) and (E) refer to the double bond configuration.

The *cis*-arrangement of the *tert*-butyl group and the NH group of the oxazolidinone was deduced from NOE studies. In addition, we obtained crystals of compound **39a** suitable for X-ray analysis (Figure 7).[27] An additional crystal structure corroborating this assignment has been published in a preliminary publication.[11b]

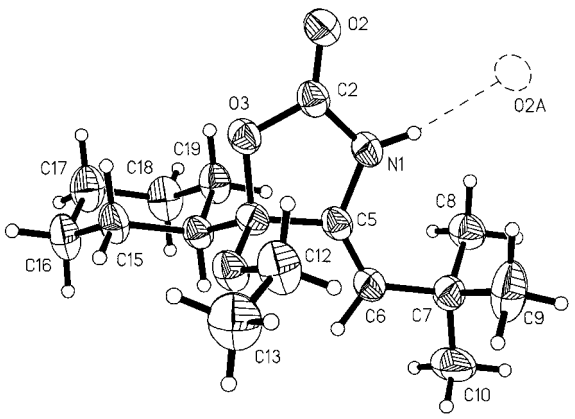
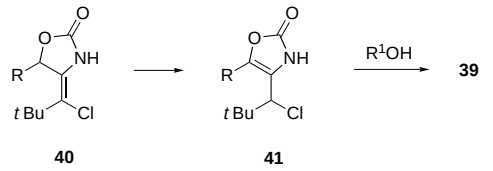


Figure 7. A molecule of compound **39a** in the crystal.

H/D-exchange experiments revealed the basic nature of the enamine structure in the products **39**.[11b] Given the steric bias of the large *tert*-butyl group and the basicity at the exocyclic methylidene carbon atom a tautomerization of the primary chloroamination product **40** appears feasible (Scheme 13).



Scheme 13. Mechanistic proposal on the formation of oxazolidinones **39**.

The resulting allylic chloride **41** can undergo solvolysis in a S_N'-fashion to yield the product **39**. Proof for the intermediacy of chloride **41** was obtained from the reaction of azide **38a** in acetonitrile. The less nucleophilic solvent facilitated the isolation of compound **41a** (R = cyclohexyl) as the product (16% yield). The reaction remained incomplete and 76% of the starting material was recovered.

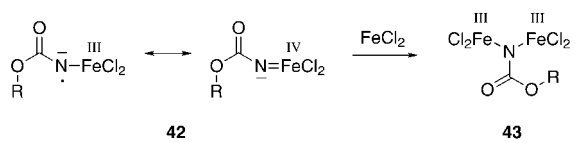
Based on this result the formation of compounds **39** can be readily explained by consecutive reactions of the chloroamination product.

Conclusion

In summary, the Fe^{II}-catalyzed intramolecular chloroamination of azidoformates is a new and widely applicable reaction for the synthesis of substituted oxazolidinones. At present, it appears as if the reaction is limited to the construction of five-membered ring compounds. Neither 3-alkenyloxycarbonyl azides nor 3-alkynyloxycarbonyl azides underwent a cyclization under the commonly used reaction conditions. The attempted reactions yielded only small amounts of the amides and recovered starting material. If 30 mol% of the catalyst were employed roughly 15% of the corresponding amide was detected.[8] As mentioned in a previous paper[7c] we rationalize the amide formation by an intermolecular attack of $FeCl_2$ at a complex **42** related to **12**/**13** (Scheme 5). The resulting μ-imido complex **43** (see Scheme 14) represents a thermodynamic valley which yields the corresponding amide upon hydrolysis.

As a direct conclusion from this hypothesis any intermediate **42** which allows only for a slow intra- or intermolecular reaction will end up as the inactive complex **43** (Scheme 14). A catalytic cycle is impossible and the nitrogen evolution slows down rather quickly.

Further studies have been initiated which aim at an improvement of the catalytic cycle based on the presented



Scheme 14. Suggested deactivation pathway of the reactive Fe-complex **42**.

results. The search for alternative metal catalysts is driven by the goal to similarly slow down the reaction to the proposed μ-imido complex and to increase the rate of the nitrogen–carbon bond formation. Other substrates are currently being tested and a chiral modification of the catalyst is being pursued. Results of this endeavour will be reported in due course.

Experimental Section

General: For general remarks, see refs. [7b, 28] Abbreviations: P = *n*-pentane, TBME = *tert*-butyl methyl ether. The azidoformates were prepared from the corresponding alcohols by a known procedure.[5b, 13] **Caution**: Azidoformates are potential explosives. Appropriate safety protection and utmost care are required while preparing and handling these compounds! The alcohols were prepared by carbonyl addition of the corresponding alkenyl and alkynyl lithium or magnesium reagents to aldehydes.[5b, 29]

General procedure for the Fe^{II}-catalyzed dediazotation: The azide (1 mmol) was dissolved in a dry solvent (5 mL) and the solution was degassed with a stream of argon for 15 min at 0 °C. Trimethyl silyl chloride (1.5 mmol) was added to the stirred solution via syringe. Solid anhydrous iron(II) chloride (0.1 mmol) was subsequently added in one portion. The solution was allowed to warm to room temperature during 21 h. Ethyl acetate (10 mL) was added and the resulting solution was washed with water (10 mL) and brine (2 × 10 mL). The organic layer was dried over magnesium sulfate and the solvent was removed in vacuo. The residue was purified by flash chromatography.

4-(1-Chloromethyl)-5-cyclohexyl-1,3-oxazolidin-2-one (7a/8a):[5a] According to the general procedure 1-azidocarbonyloxy-1-cyclohexyl-2-propene (**5a**) (209 mg, 1.00 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) **7a/8a** (156 mg, 72 %) was obtained as a colorless solid. The product was a mixture of the (4*RS*,5*SR*)- (**7a**) and (4*RS*,5*RS*)-isomer (**8a**) [*d.r.* = 91:9 (^{1}H NMR)]. The analytical data are provided for the major isomer **7a**. R_f = 0.32 (P/TBME 20:80); m.p. 115–116 °C; ^{1}H NMR (500 MHz): δ = 6.80 (s, 1H, NH), 4.07 (dd, ^3J = 4.3, ^3J = 6.0 Hz, 1H, OC*H*CHCH$_2$Cl), 3.77 (ddd, $^3J \cong {}^3J \cong {}^3J$ = 6.0 Hz, 1H, OCHC*H*CH$_2$Cl), 3.51 (dd, ^2J = 11.2, ^3J = 6.0 Hz, 1H, CH*H*Cl), 3.50 (dd, ^2J = 11.2, ^3J = 6.0 Hz, 1H, C*H*HCl), 1.90–1.45 (m, 6H, cyc-H), 1.40–0.90 (m, 5H, cyc-H); ^{13}C NMR (50 MHz): δ = 158.9 (s, C=O), 83.9 (d, O*C*HCHCH$_2$Cl), 55.9 (d, OCH*C*HCH$_2$Cl), 46.3 (t, CH$_2$Cl), 41.8 (d, cyc-CH), 27.1 (t, cyc-CH$_2$), 26.1 (t, cyc-CH$_2$), 25.7 (t, cyc-CH$_2$), 25.6 (t, cyc-CH$_2$), 25.4 (t, cyc-CH$_2$).

4-(1-Chloromethyl)-5-(2-phenylethyl)-1,3-oxazolidin-2-one (7b/8b):[5a] According to the general procedure 3-azidocarbonyloxy-5-phenyl-1-pentene (**5b**) (231 mg, 1.00 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) **7b/8b** (153 mg, 64 %) was obtained as a colorless oil. The product was a mixture of the (4*RS*,5*SR*)- (**7b**) and (4*RS*,5*RS*)-isomer (**8b**) [*d.r.* = 88:12 (^{1}H NMR)]. The analytical data are provided for the major isomer **7b**. R_f = 0.15 (P/TBME 20:80); ^{1}H NMR (300 MHz): δ = 7.36–7.16 (m, 5H, H$_{ar}$), 7.04 (s, 1H, NH), 4.36 (dt, ^3J = 5.0, ^3J = 8.5 Hz, 1H, OC*H*CHCH$_2$Cl), 3.74 (ddd, $^3J \cong {}^3J \cong {}^3J$ = 5.0 Hz, 1H, OCHC*H*CH$_2$Cl), 3.48 (d, ^3J = 5.0 Hz, 1H, CH*H*Cl), 3.46 (d, ^3J = 5.0 Hz, 1H, C*H*HCl), 2.98–2.64 (m, 2H, PhC*H*$_2$CH$_2$), 2.18–1.86 (m, 2H, PhCH$_2$C*H*$_2$); ^{13}C NMR (75 MHz): δ = 159.1 (s, C=O), 140.2 (s, C$_{ar}$), 128.6 (d, C$_{ar}$H), 128.4 (d, C$_{ar}$H), 126.3 (d, C$_{ar}$H), 79.5 (d, O*C*HCHCH$_2$Cl), 58.5 (t, OCHCH*C*H$_2$Cl), 45.6 (d, OCH*C*HCH$_2$Cl), 36.8 (t, Ph*C*H$_2$CH$_2$), 30.8 (t, PhCH$_2$*C*H$_2$).

4-(1-Chloromethyl)-5-(3-cyclohexenyl)-1,3-oxazolidin-2-one (7c/8c): According to the general procedure 1-azidocarbonyloxy-1-(3-cyclohexenyl)-2-propene (**5c**) (207 mg, 1.00 mmol) was treated with iron(II) chloride (38 mg, 0.30 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) **7c/8c** (130 mg, 60 %) was obtained as a colorless oil. The product was a mixture of the (1′*RS*,4*RS*,5*SR*)/(1′*RS*,4*RS*,5*RS*)-isomer [*d.r.* = 94:6 (^{1}H NMR)] and the (1′*SR*,4*RS*,5*SR*)/(1′*SR*,4*RS*,5*SR*)-isomer [*d.r.* = 94:6 (^{1}H NMR)]. The ratio of the pairs was determined as 44:56 (^{1}H NMR). The analytical data are provided for the major *trans*-isomers, that is, for compounds **7c**. R_f = 0.20 (P/TBME 20:80).

(1′*RS*,4*RS*,5*SR*)-*Isomer*: ^{1}H NMR (200 MHz): δ = 7.11 (s, 1H, NH), 5.65 (br s, 2H, cyc-C*H*=cyc-C*H*), 4.25 (dd, ^3J = 4.0, ^3J = 5.6 Hz, 1H, OC*H*CHCH$_2$Cl), 3.88 (dt, $^3J \cong {}^3J$ = 5.6 Hz, 1H, OCHC*H*CH$_2$Cl), 3.54 (d, ^3J = 5.6 Hz, 2H, CH$_2$Cl), 2.40–1.70 (m, 6H, cyc-H), 1.60–1.30 (m, 1H, cyc-H); ^{13}C NMR (50 MHz): δ = 159.6 (s, C=O), 127.8 (d, cyc-CH=*C*H), 125.5 (d, cyc-*C*H=CH), 83.9 (d, O*C*HCHCH$_2$Cl), 56.6 (d, OCH*C*HCH$_2$Cl), 46.6 (t, CH$_2$Cl), 38.2 (d, cyc-CH), 26.8 (t, cyc-CH$_2$), 24.9 (t, cyc-CH$_2$), 24.1 (t, cyc-CH$_2$).

(1′*SR*,4*RS*,5*SR*)-*Isomer*: ^{1}H NMR (200 MHz): δ = 7.11 (s, 1H, NH), 5.65 (br s, 2H, cyc-C*H*=cyc-C*H*), 4.25 (dd, ^3J = 4.0, ^3J = 5.6 Hz, 1H, OC*H*CHCH$_2$Cl), 3.88 (t, ^3J = 5.6 Hz, 1H, OCHC*H*CH$_2$Cl), 3.56 (d, ^3J = 5.6 Hz, 2H, CH$_2$Cl), 2.40–1.70 (m, 6H, cyc-H), 1.60–1.30 (m, 1H, cyc-H); ^{13}C NMR (50 MHz): δ = 159.6 (s, C=O), 127.3 (d, cyc-CH=*C*H), 125.0 (d, cyc-*C*H=CH), 83.4 (d, O*C*HCHCH$_2$Cl), 56.5 (d, OCH*C*HCH$_2$Cl), 46.5 (t, CH$_2$Cl), 38.2 (d, cyc-CH), 26.5 (t, cyc-CH$_2$), 24.7 (t, cyc-CH$_2$), 23.5 (t, cyc-CH$_2$); IR (film): $\tilde{\nu}$ = 3300–3250 (br, NH), 2930 (m, C$_{al}$H), 2840 (m, C$_{al}$H), 1745 (vs, C=O), 1400 (m), 1240 (m, C-O-C), 1015 (m), 740 (w), 650 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 215 (17) $[M]^+$, 93 (50) $[C_7H_9]^+$, 91 (41), 81 (39) $[C_6H_9]^+$, 80 (56) $[C_6H_8]^+$, 79 (85) $[C_6H_7]^+$, 78 (100) $[C_6H_6]^+$; elemental analysis calcd (%) for $C_{10}H_{14}NO_2Cl$ (215.68): C 55.69, H 6.54, N 6.49; found: C 55.48, H 6.70, N 6.37.

4-(1-Chloromethyl)-5-heptyl-1,3-oxazolidin-2-one (7d/8d): According to the general procedure 3-azidocarbonyloxy-1-decene (**5d**) (225 mg, 1.00 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) **7d/8d** (138 mg, 60 %) was obtained as a colorless oil. The product was a mixture of the (4*RS*,5*SR*)- (**7d**) and (4*RS*,5*RS*)-isomer (**8d**) [*d.r.* = 88:12 (^{1}H NMR)]. The analytical data are provided for the major isomer **7d**. R_f = 0.32 (P/TBME 20:80); ^{1}H NMR (300 MHz): δ = 6.82 (s, 1H, NH), 4.36 (dt, ^3J = 5.3, ^3J = 7.2 Hz, 1H, OC*H*CHCH$_2$Cl), 3.74 (ddd, $^3J \cong {}^3J \cong {}^3J$ = 5.3 Hz, 1H, OCHC*H*CH$_2$Cl), 3.54 (d, ^3J = 5.3 Hz, 1H, CH*H*Cl), 3.52 (d, ^3J = 5.3 Hz, 1H, C*H*HCl), 1.90–1.00 (m, 12H, CH$_3$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$), 0.78 (t, ^3J = 6.5 Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): δ = 159.0 (s, C=O), 80.3 (d, O*C*HCHCH$_2$Cl), 58.4 (t, OCHCH*C*H$_2$Cl), 45.6 (d, OCH*C*HCH$_2$Cl), 35.0 (t, CH$_2$), 31.6 (t, CH$_2$), 29.1 (t, CH$_2$), 29.0 (t, CH$_2$), 24.4 (t, CH$_2$), 22.5 (t, CH$_3$*C*H$_2$), 14.0 (q, CH$_3$); IR (film): $\tilde{\nu}$ = 3300–3250 (br, NH), 2930 (vs, C$_{al}$H), 2855 (s, C$_{al}$H), 1750 (vs, C=O), 1235 (m, C-O-C), 985 (w), 730 cm^{-1} (w); MS (EI, 70eV): *m*/*z* (%): 184 (100) $[M - CH_2Cl]^+$, 168 (6), 140 (11), 81 (20) $[C_6H_9]^+$, 67 (23) $[C_5H_7]^+$, 56 (42) $[C_4H_8]^+$, 55 (89) $[C_4H_7]^+$, 43 (49), 41 (57) $[C_3H_5]^+$; elemental analysis calcd (%) for $C_{11}H_{20}NO_2Cl$ (233.74): C 56.52, H 8.62, N 5.99; found: C 56.55, H 8.62, N 5.97.

4-(1-Chloromethyl)-5-(1-methylethyl)-1,3-oxazolidin-2-one (7e/8e): According to the general procedure 3-azidocarbonyloxy-4-methyl-1-pentene (**5e**) (170 mg, 1.00 mmol) was treated with iron(II) chloride (38 mg, 0.30 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) **7e/8e** (58 mg, 33 %) was obtained as a colorless solid. The product was a mixture of the (4*RS*,5*SR*)- (**7e**) and (4*RS*,5*RS*)-isomer (**8e**) [*d.r.* = 92:8 (^{1}H NMR)]. The analytical data are provided for the major isomer **7e**. M.p. 65–67 °C; ^{1}H NMR (200 MHz): δ = 6.80 (s, 1H, NH), 4.07 (dd, ^3J = 6.4, ^3J = 5.5 Hz, 1H, OC*H*CHCH$_2$Cl), 3.74 (ddd, $^3J \cong {}^3J \cong {}^3J$ = 5.5 Hz, 1H, OCHC*H*CH$_2$Cl), 3.47 (d, ^3J = 5.5 Hz, 2H, CH$_2$Cl), 1.88 (dqq, $^3J \cong {}^3J \cong {}^3J$ = 6.4 Hz, 1H, CH$_3$C*H*CH$_3$), 0.92 (d, ^3J = 6.4 Hz, 3H, CH$_3$CHC*H*$_3$), 0.90 (d, ^3J = 6.4 Hz, 3H, C*H*$_3$CHCH$_3$); ^{13}C NMR (75 MHz): δ = 159.1 (s, C=O), 84.5 (d, OCHCHCH$_2$Cl), 55.9 (d, *C*HCH$_2$Cl), 46.3 (t, CH$_2$Cl), 32.2 (d, CH$_3$*C*HCH$_3$), 17.2 (q, CH$_3$), 16.6 (q, CH$_3$); IR (KBr): $\tilde{\nu}$ = 3300–3250 (br, NH), 2970 (m, C$_{al}$H), 2930 (m, C$_{al}$H), 2880 (m, C$_{al}$H), 1750 (vs, C=O), 1240 (m, C-O-C), 960 (m), 655 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 128 (100) $[M - CH_2Cl]^+$, 90 (20), 86 (26) $[C_3H_3NO_2]^+$, 84 (31), 57 (50) $[C_4H_9]^+$, 55 (23) $[C_4H_7]^+$, 43 (46) $[C_3H_7]^+$, 42 (46) $[C_3H_6]^+$, 41 (75) $[C_3H_5]^+$, 29 (36) $[C_2H_5]^+$, 27 (53) $[C_2H_3]^+$; elemental analysis calcd (%) for $C_7H_{12}NO_2Cl$ (177.63): C 47.33, H 6.81, N 7.88; found: C 47.78, H 6.87, N 7.63.

4-(1-Chloromethyl)-5-(prop-2-enyl)-1,3-oxazolidin-2-one (7f/8f): According to the general procedure 3-azidocarbonyloxy-1,5-hexadiene (**5f**) (334 mg, 2.00 mmol) was treated with iron(II) chloride (26 mg, 0.20 mmol)

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and trimethyl silyl chloride (0.38 mL, 3.00 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) **7f/8f** (239 mg, 68%) was obtained as a yellow oil. The product was a mixture of the (4*RS*,5*SR*)- (**7f**) and (4*RS*,5*RS*)-isomer (**8f**) [*d.r.* = 90:10 (^{1}H NMR)]. The analytical data are provided for the major isomer **7f**. $R_f = 0.20$ (P/TBME 20:80); ^{1}H NMR (300 MHz): $\delta = 7.25$ (br s, 1H, NH), 5.83 (ddt, $^3J = 6.0$, $^3J_{cis} = 10.1$, $^3J_{trans} = 17.1$ Hz, 1H, OCHCH$_2$C*H*CH$_2$), 5.28 (d, $^3J_{trans} = 17.1$ Hz, 1H, CHCH*H*$_{trans}$), 5.26 (d, $^3J_{cis} = 10.1$ Hz, 1H, CHC*H*$_{cis}$H), 4.58 (dt, $^3J \cong {}^3J = 6.0$ Hz, 1H, OCH), 3.92 (dt, $^3J \cong {}^3J = 6.0$ Hz, 1H, HN*CH*), 3.68 (d, $^3J = 6.0$ Hz, 2H, CH$_2$Cl), 2.60 (dd, $^3J \cong {}^3J = 6.0$ Hz, 2H, OCHC*H*$_2$CH); ^{13}C NMR (75 MHz): $\delta = 158.9$ (s, C=O), 130.7 (d, CH$_2$*C*HCH$_2$), 119.8 (t, *C*H$_2$CHCH$_2$), 78.8 (d, OCH), 57.1 (d, HN*C*H), 45.5 (t, CH$_2$Cl), 38.7 (t, OCH*C*H$_2$CH); IR (film): $\tilde{\nu} = 3300-3250$ (br, NH), 2980 (m, C$_{al}$H), 2940 (m, C$_{al}$H), 1755 (vs, C=O), 1400 (m), 1240 (m, C-O-C), 1060 (m), 990 (m), 950 (m), 730 cm^{-1} (w); MS (EI, 70eV): *m*/*z* (%): 134 (100) [$M - C_3H_5$]$^+$, 126 (48) [$M - CH_2Cl$]$^+$, 90 (35), 86 (30) [$C_3H_3NO_2$]$^+$, 84 (49) [$C_3H_2NO_2$]$^+$, 63 (37), 49 (15) [CH_2Cl]$^+$, 41 (31) [C_3H_5]$^+$, 28 (95) [CO]$^+$; elemental analysis calcd (%) for $C_7H_{10}NO_2Cl$ (175.61): C 47.88, H 5.74, N 7.98; found: C 47.65, H 5.59, N 7.94.

4-(1-Chlorobutyl)-1,3-oxazolidin-2-one (**10a/11a**): According to the general procedure *trans*-1-azidocarbonyloxy-2-hexene (**9a**) (169 mg, 1.00 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). After work-up **10a/11a** (150 mg, 84%) was obtained as a colorless oil. The product was a mixture of the (4*RS*,1′*SR*)- (**10a**) and (4*RS*,1′*RS*)-isomer (**11a**) [*d.r.* = 49:51 (^{1}H NMR)].

Thermal decomposition: *trans*-1-Azidocarbonyloxy-2-hexene (**9a**) (500 mg, 2.96 mmol) was dissolved in 1,1,2,2-tetrachloroethane (50 mL) and heated to 150 °C for 4 h. After the reaction mixture was cooled most of the solvent was removed in vacuo. A brown oil (800 mg) was obtained. By integration of the ^{1}H NMR signals the approximate yield could be estimated (62%). **11a** was obtained in diastereomerically pure form [*d.r.* > 95:5 (^{1}H NMR)].

(4*RS*,1′*SR*)-*Isomer* (**10a**): ^{1}H NMR (200 MHz): $\delta = 7.40$ (s, 1H, NH), 4.42 (dd, $^2J \cong {}^3J = 9.0$ Hz, 1H, OCH*H*CH), 4.23 (dd, $^2J = 9.0$, $^3J = 5.0$ Hz, 1H, OC*H*HCH), 4.04 (br ddd, $^3J \cong {}^3J = 5.0$, $^3J = 9.0$ Hz, 1H, OCH$_2$C*H*), 3.87–3.75 (m, 1H, CHCl), 1.80–1.30 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 0.95 (t, $^3J = 7.1$ Hz, 3H, CH$_3$); ^{13}C NMR (50 MHz): $\delta = 160.4$ (s, C=O), 67.7 (t, O*C*H$_2$CH), 64.2 (d, OCH$_2$*C*H), 57.5 (d, CHCl), 35.5 (t, *C*H$_2$CH$_2$CH$_3$), 19.9 (t, *C*H$_2$CH$_3$), 13.7 (q, CH$_3$).

(4*RS*,1′*RS*)-*Isomer* (**11a**): ^{1}H NMR (200 MHz): $\delta = 7.05$ (s, 1H, NH), 4.46 (dd, $^2J \cong {}^3J = 9.0$ Hz, 1H, OCH*H*CH), 4.28 (dd, $^2J = 9.0$, $^3J = 5.0$ Hz, 1H, OC*H*HCH), 3.93 (br ddd, $^3J \cong {}^3J = 5.0$, $^3J = 9.0$ Hz, 1H, OCH$_2$C*H*), 3.87–3.75 (m, 1H, CHCl), 1.80–1.30 (m, 4H, C*H*$_2$C*H*$_2$CH$_3$), 0.95 (t, $^3J = 7.1$ Hz, 3H, CH$_3$); ^{13}C NMR (50 MHz): $\delta = 160.7$ (s, C=O), 68.5 (t, O*C*H$_2$CH), 64.3 (d, OCH$_2$*C*H), 57.6 (d, CHCl), 36.1 (t, *C*H$_2$CH$_2$CH$_3$), 19.5 (t, *C*H$_2$CH$_3$), 13.7 (q, CH$_3$); IR (film): $\tilde{\nu} = 3300-3250$ (br, NH), 2960 (m, C$_{al}$H), 2930 (w, C$_{al}$H), 2875 (w, C$_{al}$H), 1750 (vs, C=O), 1230 (m, C-O-C), 1030 (m), 940 (w), 765 cm^{-1} (w); MS (EI, 70eV): *m*/*z* (%): 86 (100) [$C_3H_3NO_2$]$^+$, 55 (28) [C_4H_7]$^+$, 49 (37), 47 (41), 41 (23), 35 (29); elemental analysis calcd (%) for $C_7H_{12}NO_2Cl$ (177.63): C 47.33, H 6.81, N 7.88; found: C 47.40, H 6.57, N 7.72.

(4*RS*,1′*RS*)4-(1-Chloro-1-phenylmethyl)-1,3-oxazolidin-2-one (10b): According to the general procedure *trans*-1-azidocarbonyloxy-3-phenyl-2-propene (**9b**) (203 mg, 1.00 mmol) was treated with iron(II) chloride (38 mg, 0.30 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) **10b** (161 mg, 76%) was obtained as a colorless solid. $R_f = 0.26$ (P/TBME 20:80); m.p. 85–90 °C; ^{1}H NMR (200 MHz): $\delta = 7.50-7.25$ (m, 5H, H$_{ar}$), 5.95 (s, 1H, NH), 4.82 (d, $^3J = 8.5$ Hz, 1H, CHCl), 4.34 (ddd, $^3J = 4.7$, $^3J = 8.5$, $^3J = 8.5$ Hz, 1H, CHN), 4.24 (dd, $^2J = 8.5$, $^3J = 8.5$ Hz, 1H, CH*H*O), 4.03 (dd, $^2J = 8.5$ Hz, $^3J = 4.7$ Hz, 1H, C*H*HO); ^{13}C NMR (50 MHz): $\delta = 158.9$ (s, C=O), 135.9 (s, C$_{ar}$), 129.4 (d, C$_{ar}$H), 129.0 (d, C$_{ar}$H), 127.5 (d, C$_{ar}$H), 66.9 (t, CH$_2$O), 64.8 (d, CHCl), 58.6 (d, CHN); IR (KBr): $\tilde{\nu} = 3300-3250$ (br, NH), 3035 (w, C$_{ar}$H), 2960 (w, C$_{al}$H), 2930 (w, C$_{al}$H), 1775 (vs, C=O), 1450 (w), 1400 (w), 1245 (m, C-O-C), 1230 (m), 1045 (m), 1025 (m), 765 (w), 690 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 125 (14) [C_7H_6Cl]$^+$, 91 (11) [C_7H_7]$^+$, 86 (100) [$C_3H_3NO_2$]$^+$, 77 (4) [C_6H_5]$^+$, 42 (32) [HNCO]$^+$; elemental analysis calcd (%) for $C_{10}H_{10}NO_2Cl$ (211.65): C 56.75, H 4.76, N 6.62; found: C 56.48, H 4.93, N 6.57.

(4*RS*,1′*SR*)-4-(1-Chloro-1-phenylmethyl)-1,3-oxazolidin-2-one (11b): *trans*-1-Azidocarbonyloxy-3-phenyl-2-propene (**9b**) (610 mg, 3.00 mmol) was dissolved in 1,1,2,2-tetrachloroethane (30 mL) and heated to 150 °C for 3 h. After cooling the solvent was removed in vacuo and the residue was purified by chromatography (P/TBME 20:80). **11b** (265 mg, 42%) was obtained as a colorless solid. $R_f = 0.14$ (P/TBME 20:80); m.p. 135–145 °C; ^{1}H NMR (200 MHz): $\delta = 7.70-7.40$ (m, 5H, H$_{ar}$), 5.90 (s, 1H, NH), 4.89 (d, $^3J = 8.5$ Hz, 1H, CHCl), 4.66 (dd, $^2J \cong {}^3J = 8.5$ Hz, 1H, CH*H*O), 4.58 (dd, $^2J = 8.5$, $^3J = 5.0$ Hz, 1H, C*H*HO), 4.40 (ddd, $^3J = 5.0$, $^3J \cong {}^3J = 8.5$ Hz, 1H, CHN); ^{13}C NMR (50 MHz): $\delta = 158.7$ (s, C=O), 136.4 (s, C$_{ar}$), 129.4 (d, C$_{ar}$H), 129.1 (d, C$_{ar}$H), 127.6 (d, C$_{ar}$H), 68.1 (t, CH$_2$O), 63.5 (d, CHCl), 58.2 (d, CHN); IR (KBr): $\tilde{\nu} = 3300-3250$ (br, NH), 3140 (w, C$_{ar}$H), 1735 (vs, C=O), 1450 (w), 1410 (w), 1250 (m, C-O-C), 1030 (m), 705 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 125 (7) [C_7H_6Cl]$^+$, 91 (7) [C_7H_7]$^+$, 86 (100) [$C_3H_3NO_2$]$^+$, 77 (2) [C_6H_5]$^+$, 42 (19) [HNCO]$^+$; elemental analysis calcd (%) for $C_{10}H_{10}NO_2Cl$ (211.65): C 56.75, H 4.76, N 6.62; found: C 56.48, H 4.93, N 6.57.

(4*RS*,5*SR*,1′*RS*)-4-(1-Chloro-1-phenylmethyl)-5-methyl-1,3-oxazolidin-2-one (19): According to the general procedure (1*E*)-3-azidocarbonyloxy-1-butene (**18**) (217 mg, 1.00 mmol) was treated with iron(II) chloride (38 mg, 0.30 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) the product (36 mg, 16%) was obtained as a yellow solid. The product was a mixture of the (4*RS*,5*SR*,1′*RS*) (**19**) and the (4*RS*,5*SR*,1′*SR*) isomer [*d.r.* = 75:25 (^{1}H NMR)]. Analytical data are provided for the major isomer. $R_f = 0.25$; m.p. 113–117 °C; ^{1}H NMR (300 MHz): $\delta = 7.42-7.34$ (m, 5H, H$_{ar}$), 6.09 (br s, 1H, NH), 4.75 (d, $^3J = 8.9$ Hz, 1H, CHCl), 4.25 (dq, $^3J = 6.1$, $^3J = 5.2$ Hz, 1H, CH$_3$C*H*), 3.86 (br dd, $^3J = 5.2$, $^3J = 8.9$ Hz, 1H, CH$_3$CHC*H*CHCl), 1.05 (d, $^3J = 6.1$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): δ = signal for C=O not observed, 135.9 (s, C$_{ar}$), 129.6 (d, C$_{ar}$H), 129.2 (d, C$_{ar}$H), 127.7 (d, C$_{ar}$H), 75.6 (d, CHO), 65.6 (d, CHNH), 65.2 (d, CHCl), 15.1 (q, CH$_3$); IR (KBr): $\tilde{\nu} = 3300-3200$ (br, NH), 3140 (w, C$_{ar}$H), 2980 (w, C$_{al}$H), 2930 (w, C$_{al}$H), 1785 (vs, C=O), 1730 (vs), 1380 (m), 1240 (s, C-O-C), 1075 (m), 1045 (m), 980 (m), 720 cm^{-1} (s); MS (EI, 70eV): *m*/*z* (%): 167 (< 1) [$M - CH_3 - Cl$]$^+$, 149 (1), 125 (27) [C_7H_6Cl]$^+$, 100 (100) [$M - C_7H_6Cl$]$^+$, 91 (22) [C_7H_7]$^+$, 77 (6) [C_6H_5]$^+$, 56 (78), 28 (35) [CO]$^+$; elemental analysis calcd (%) for $C_{11}H_{12}NO_2Cl$ (225.67): C 58.55, H 5.36, N 6.21; found: C 58.53, H 5.38, N 5.99.

(1*RS*,2*SR*,6*RS*)-9-Aza-2-chloro-7-oxabicyclo[4.3.0]nonan-8-one (21): According to the general procedure 3-azidocarbonyloxycyclohex-1-ene (**20**) (254 mg, 1.52 mmol) was treated with iron(II) chloride (58 mg, 0.30 mmol) and trimethyl silyl chloride (0.30 mL, 2.25 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) **21** (125 mg, 47%) was obtained as a colorless solid. $R_f = 0.13$ (P/TBME 30:70); m.p. 120–126 °C; ^{1}H NMR (200 MHz): $\delta = 5.90$ (s, 1H, NH), 4.73 (td, $^3J = 5.0$, $^3J = 7.2$ Hz, 1H, CHO), 4.22 (dd, $^3J = 4.0$, $^3J = 7.2$ Hz, 1H, CHN), 4.07 (ddd, $^3J = 4.0$, $^3J = 5.6$, $^3J = 10.3$ Hz, 1H, CHCl), 2.10–1.60 (m, 6H, C*H*$_2$CH$_2$C*H*$_2$); ^{13}C NMR (50 MHz): $\delta = 159.0$ (s, C=O), 75.5 (d, CHO), 57.1 (d, CHCl), 56.1 (d, CHN), 27.8 (t, *C*H$_2$CHO), 25.2 (t, CHCl*C*H$_2$CH$_2$), 18.1 (t, CH$_2$C*H*$_2$CH$_2$); IR (KBr): $\tilde{\nu} = 3250-3200$ (br, NH), 2950 (w, C$_{al}$H), 1765 (vs, C=O), 1400 (s), 1310 (s), 1295 (s, C-O-C), 1240 (s), 1050 (s), 1010 (s), 940 (s), 785 (m), 750 (m), 720 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 177 (10) [$M(^{37}Cl)$]$^+$, 175 (30) [$M(^{35}Cl)$]$^+$, 140 (< 1) [$M - Cl$]$^+$, 98 (98) [$C_6H_{10}O$]$^+$, 85 (12) [$C_3H_2NO_2$]$^+$, 68 (24), 54 (27), 41 (60) [C_3H_5]$^+$, 39 (30); elemental analysis calcd (%) for $C_7H_{10}NO_2Cl$ (175.61): C 47.88, H 5.74, N 7.98; found: C 47.49, H 5.75, N 7.67.

4-(1-Chloroethyl)-5-(prop-2-enyl)-1,3-oxazolidin-2-one (23): According to the general procedure (5*E*)-4-azidocarbonyloxy-1,5-heptadiene (**22**) (362 mg, 2.00 mmol) was treated with iron(II) chloride (26 mg, 0.20 mmol) and trimethyl silyl chloride (0.38 mL, 3.00 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) the product (243 mg, 64%) was obtained as a yellow oil in a mixture of the 4,5-*trans*-isomers (**23**) and 4,5-*cis*-isomers [*d.r.* = 92:8, epimeric ratio: 65:35 (^{1}H NMR)]. The analytical data are provided for the (4*RS*,5*SR*,1′*SR*) isomer. $R_f = 0.21$ (P/TBME 20:80); ^{1}H NMR (300 MHz): $\delta =$ 7.71 (s, 1H, NH), 5.97–5.81 (m, 1H, CH$_2$C*H*CH$_2$CHO), 5.34 (br d, $^3J_{trans} = 17.1$ Hz, CHCH*H*$_{trans}$), 5.32 (br d, $^3J_{cis} = 10.2$ Hz, 1H, CHC*H*$_{cis}$H), 4.70–4.58 (m, 1H, OCH), 4.05 (dq, $^3J \cong {}^3J = 6.3$ Hz, 1H, CHCl), 3.66 (dd, $^3J = 4.0$ Hz, $^3J = 6.3$ Hz, 1H, NHC*H*), 2.61 (dd, $^3J \cong {}^3J = 6.0$ Hz, 2H, OCHC*H*$_2$CH), 1.61 (d, $^3J = 6.3$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): $\delta = 159.4$ (s, C=O), 130.9 (d, CH$_2$*C*HCH$_2$CHO), 119.7 (t, *C*H$_2$CHCH$_2$CHO), 79.0 (d, OCH), 62.1 (d, CHCl), 58.3 (d, HNCH), 39.2 (t, OCH*C*H$_2$), 20.6 (q, CH$_3$); IR (film): $\tilde{\nu} = 3300-3250$ (br, NH), 2980 (m, C$_{al}$H), 2935 (m, C$_{al}$H), 1755 (vs, C=O), 1400 (m), 1240 (m, C-O-C), 1060

(m), 995 (m), 925 (m), 735 (w), 685 cm^{-1} (w); MS (EI, 70eV): *m/z* (%): 148 (30) $[M-C_3H_5]^+$, 126 (100) $[M-C_2H_4Cl]^+$, 84 (11) $[C_3H_2NO_2]^+$, 55 (30), 41 (45) $[C_3H_5]^+$, 28 (72) $[CO]^+$; elemental analysis calcd (%) for $C_8H_{12}NO_2Cl$ (189.64): C 50.63, H 6.38, N 7.39; found: C 50.59, H 6.16, N 7.01.

3-Azidocarbonyloxy-cycloocta-1,5-diene (24): 1,5-Cyclooctadien-3-ol[30] (3.65 g, 29.4 mmol) was dissolved in benzene (100 mL). Pyridine (8.37 g, 8.55 mL, 105.0 mmol) and 1,1′-carbonyldiimidazole (10.8 g, 66.0 mmol) were added. The mixture was stirred at room temperature for 4 h. Ethyl acetate (150 mL) was added and the slurry was washed with brine (2 × 50 mL). The organic layer was dried over magnesium sulfate. The solvent was removed in vacuo and the resulting residue was dissolved in *N*,*N*′-dimethylformamide (100 mL). Sodium azide (10.71 g, 105.0 mmol) was added and the pH was adjusted to 4 by addition of concentrated hydrochloric acid (ca. 15 mL). The slurry was stirred at room temperature for 18 h. Ethyl acetate (100 mL) was added and the mixture was washed with brine (3 × 150 mL). The aqueous layer was extracted with ethyl acetate (2 × 150 mL) and the combined organic layers were dried over magnesium sulfate. The solvent was removed in vacuo and the residue was purified by flash chromatography (P/TBME 20:80). Compound **24** (4.84 g, 85%) was isolated as a yellow liquid. $R_f = 0.67$ (P/TBME 20:80); ^{1}H NMR (500 MHz): $\delta = 5.91$ (dddd, $^3J = 9.8$, $^3J = 5.0$, $^3J = 7.0$, $^5J = 1.0$ Hz, 1H, OCH), 5.67 (dddd, $^3J = 12.4$, $^3J = 5.4$, $^3J = 7.0$, $^5J = 1.8$ Hz, 1H, OCHCHC*H*), 5.59 (ddddd, $^3J = 11.8$, $^3J \cong {}^3J = 6.4$, $^4J = 0.9$, $^5J = 1.8$ Hz, 1H, OCHCH$_2$CHC*H*), 5.51 (dddd, $^3J = 12.4$, $^3J \cong {}^3J = 5.0$, $^5J = 1.9$ Hz, 1H, OCHC*H*), 5.48 (dddd, $^3J = 11.8$, $^3J = 5.3$, $^4J = 0.9$, $^5J = 1.9$ Hz, 1H, OCHCH$_2$C*H*), 2.73 (dddd, $^2J = 16.0$, $^3J \cong {}^3J = 5.0$, $^5J = 0.8$ Hz, 1H, OCHCH*H*), 2.48 (ddd, $^2J = 16.0$, $^3J = 7.0$, $^3J = 9.8$ Hz, 1H, OCHC*H*H), 2.44 (ddd, $^2J = 8.0$, $^3J = 5.3$, $^5J = 0.8$ Hz, 1H, OCHCHCHCH$_2$C*H*H), 2.39 (ddd, $^2J = 10.9$, $^3J = 5.1$, $^5J = 0.8$ Hz, 1H, OCHCHCHC*H*H), 2.29 (m, 1H, OCHCHCHCH*H*), 2.18 (m, 1H, OCHCHCHCH$_2$CH*H*); ^{13}C NMR (125 MHz): $\delta = 156.9$ (s, C=O), 130.1 (d, OCHCH*C*H), 130.0 (d, OCHCH$_2$CH*C*H), 127.5 (d, OCHCH$_2$*C*H), 124.4 (d, OCH*C*H), 77.2 (d, O*C*H), 33.5 (t, OCH*C*H$_2$), 27.8 (t, OCHCHCH*C*H$_2$), 27.7 (t, OCHCH$_2$CHCH*C*H$_2$); IR (film): $\tilde{\nu} = 2950$ (w, C_{al}H), 2895 (w, C_{al}H), 2190 (s, N_3), 2135 (s, N_3), 1725 (vs, C=O), 1240 cm^{-1} (vs, C-O-C); MS (EI, 70eV): *m/z* (%): 165 (14) $[M-N_2]^+$, 107 (31) $[M-OCON_3]^+$, 106 (38) $[M-HOCON_3]^+$, 80 (43), 79 (74), 70 (47), 67 (60), 54 (100) $[C_4H_6]^+$, 53 (30), 41 (58), 39 (54), 28 (85) $[N_2, CO]^+$; elemental analysis calcd (%) for $C_9H_{11}N_3O_2$ (193.20): C 55.95, H 5.74, N 21.75; found: C 56.48, H 5.80, N 21.24.

(1*RS*,2*RS*,8*SR*)-2-Chloro-9-oxa-11-azabicyclo[6.3.0]undec-5-en-10-one (25): According to the general procedure 3-azidocarbonyloxycycloocta-1,5-diene (**24**) (193 mg, 1.00 mmol, purity: 88%) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 30:70) **25** (100 mg, 58%) was obtained as a colorless solid. $R_f = 0.25$ (P/TBME 30:70), m.p. 98–105 °C; ^{1}H NMR (500 MHz): $\delta = 6.20$ (s, 1H, NH), 5.66 (dddd, $^3J \cong {}^3J \cong {}^3J = 9.1$, $^4J = 1.3$ Hz, 1H, C*H*CHCH$_2$CHO), 5.45 (m, 1H, CHC*H*CH$_2$CHO), 4.88 (ddd, $^3J = 5.0$, $^3J = 7.1$, $^3J = 11.9$ Hz, 1H, CHO), 3.98 (dt, $^3J = 6.5$, $^3J = 10.3$ Hz, 1H, CHCl), 3.87 (dd, $^3J = 7.1$, $^3J = 10.3$ Hz, 1H, CHClC*H*CHO), 2.86 (d, $^3J = 6.5$ Hz, 1H, CH*H*CHCl), 2.48–2.32 (m, 2H, C*H*$_2$CHO), 2.24–2.12 (m, 1H, CH*H*CH$_2$CHCl), 2.04–1.93 (m, 1H, C*H*HCH$_2$CHCl), 1.84–1.75 (m, 1H, C*H*HCHCl); ^{13}C NMR (125 MHz): $\delta = 157.2$ (s, C=O), 129.7 (d, *C*HCHCH$_2$CHO), 124.2 (d, CH*C*HCH$_2$CHO), 78.2 (d, CHO), 63.9 (d, CHCl), 63.0 (d, CHNH), 36.4 (t, *C*H$_2$CHO), 35.0 (t, *C*H$_2$CHCl), 23.9 (t, *C*H$_2$CH$_2$CHCl); IR (KBr): $\tilde{\nu} =$ 3300–3250 (br, NH), 2940 (m, C_{al}H), 1745 (vs, C=O), 1400 (m), 1295 (m, C-O-C), 1250 (m), 1030 (m), 900 (m), 700 cm^{-1} (m); MS (EI, 70eV): *m/z* (%): 203 (16) $[M(^{37}Cl)]^+$, 201 (43) $[M(^{35}Cl)]^+$, 166 (50) $[M-Cl]^+$, 124 (41) $[C_8H_{12}O]^+$, 95 (30), 94 (31), 85 (74) $[C_3H_3NO_2]^+$, 68 (40), 67 (43), 54 (89), 53 (47), 41 (59) $[C_3H_5]^+$, 39 (53); elemental analysis calcd (%) for $C_9H_{12}NO_2Cl$ (201.65): C 53.61, H 6.00, N 6.95; found: C 53.46, H 5.87, N 6.69.

(1*RS*,2*RS*,3*RS*)-2-Chloro-9-oxa-11-azabicyclo[6.3.0]undec-5-en-10-one (26): 3-Azidocarbonyloxycycloocta-1,5-diene (483 mg, 2.50 mmol, purity: 88%) (**24**) was dissolved in 1,1,2,2-tetrachloroethane (50 mL) and heated to 150 °C for 2 h. After cooling the solvent was removed in vacuo and the residue was purified by chromatography (P/TBME 20:80). **26** (65 mg, 16%) was obtained as a colorless solid. $R_f = 0.21$ (P/TBME 20:80); m.p. 108–115 °C; ^{1}H NMR (500 MHz): $\delta = 5.69$ (dtt, $^3J = 7.7$, 11.3, $^4J = 1.7$ Hz, 1H, C*H*CHCH$_2$CHO), 5.59 (dt, $^3J = 5.0$, 11.3 Hz, 1H, CHC*H*CH$_2$CHO), 5.52 (s, 1H, NH), 5.05 (ddd, $^3J = 5.0$, 7.0, 12.1 Hz, 1H, CHO), 4.28 (dt, $^3J = 4.1$, 10.7 Hz, 1H, CHCl), 4.04 (dd, $^3J = 7.0$, 10.7 Hz, 1H, CHClC*H*CHO), 2.66 (br ddd, $^2J = 17.3$, $^3J = 5.0$, 12.1 Hz, 1H, CHCH*H*CHO), 2.57 (br ddd, $^2J =$ 17.3, $^3J \cong {}^3J = 5.0$ Hz, 1H, CHC*H*HCHO), 2.31 (ddt, $^2J = 11.5$, $^3J = 4.1$, 13.9 Hz, 1H, CH*H*CHCl), 2.24–2.12 (m, 2H, C*H*$_2$CH$_2$CHCl), 1.91 (ddt, $^2J = 11.5$, $^3J = 4.1$, 5.8 Hz, 1H, C*H*HCHCl); ^{13}C NMR (125 MHz): $\delta = 157.3$ (s, C=O), 127.9 (d, *C*HCHCH$_2$CHO), 126.2 (d, CH*C*HCH$_2$CHO), 77.2 (d, CHO), 61.6 (d, CHNH), 60.4 (d, CHCl), 37.3 (t, *C*H$_2$CHCl), 31.0 (t, *C*H$_2$CHO), 23.7 (t, *C*H$_2$CH$_2$CHCl); IR (KBr): $\tilde{\nu} = 3300-3250$ (br, NH), 2940 (m, C_{al}H), 1770 (vs, C=O), 1470 (m), 1365 (m), 1220 (s), 1030 (m), 980 (m), 730 cm^{-1} (m); MS (EI, 70eV): *m/z* (%): 201 (14) $[M]^+$, 166 (8) $[M-Cl]^+$, 124 (77) $[C_8H_{12}O]^+$, 94 (21), 86 (47) $[C_3H_4NO_2]^+$, 85 (100) $[C_3H_3NO_2]^+$, 68 (35), 67 (25), 54 (52), 41 (21) $[C_3H_5]^+$, 39 (18); elemental analysis calcd (%) for $C_9H_{12}NO_2Cl$ (201.65): C 53.61, H 6.00, N 6.95; found: C 53.39, H 5.84, N 6.92.

(4*RS*,5*SR*)-4-Methyl-5-(prop-2-enyl)-1,3-oxazolidin-2-one (27):[31] (4*RS*,5*SR*)-4-(1-Chloromethyl)-5-(prop-2-enyl)-1,3-oxazolidin-2-one (**7f**) (649 mg, 3.70 mmol) was dissolved in benzene (50 mL). The solution was degassed with a stream of argon for 15 min and subsequently heated to reflux. A solution of tri-*n*-butyl tinhydride (1.40 g, 4.80 mmol) and *N*,*N*′-*bis*-azoisobutyronitrile (50 mg) in dry benzene (20 mL) was added during a period of 30 min. The solution was heated under reflux for 3 h. After cooling the solvent was removed in vacuo and the residue was purified by flash chromatography (P/TBME 10:90). Compound **27** (415 mg, 72%) was obtained as a colorless oil. $R_f = 0.23$ (P/TBME 10:90); ^{1}H NMR (200 MHz): $\delta = 6.80$ (s, 1H, NH), 5.78–5.65 (m, 1H, CH$_2$C*H*CH$_2$), 5.12 (d, $^3J_{trans} =$ 17.1 Hz, 1H, CHCH*H*$_{trans}$), 5.10 (d, $^3J_{cis} = 10.0$ Hz, 1H, CHCH$_{cis}$H), 4.08 (dt, $^3J \cong {}^3J = 6.0$ Hz, 1H, CH$_3$CHC*H*), 3.57 (dq, $^3J \cong {}^3J = 6.0$ Hz, 1H, CH$_3$C*H*), 2.48–2.30 (m, 2H, CHC*H*$_2$CHO), 1.19 (d, $^3J = 6.0$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): $\delta = 159.4$ (s, C=O), 131.4 (d, CH$_2$*C*HCH$_2$CHO), 119.0 (t, *C*H$_2$CHCH$_2$CHO), 82.8 (d, CHO), 52.6 (d, CHNH), 38.8 (t, *C*H$_2$CHO), 20.5 (q, CH$_3$).

(1*RS*,2*SR*)-9-Oxa-11-azabicyclo[6.3.0]undec-5-en-10-one (28): As described for the conversion **7f** → **27** (1*RS*,2*RS*,8*SR*)-2-chloro-9-oxa-11-azabicyclo[6.3.0]undec-5-en-10-one (**25**) (202 mg, 1.00 mmol) and tri-*n*-butyltinhydride (392 mg, 1.35 mmol) were allowed to react for 4 h. After chromatographic purification (P/TBME 20:80) **28** (120 mg, 72%) was obtained as a colorless oil. $R_f = 0.17$ (P/TBME 20:80); ^{1}H NMR (200 MHz): $\delta = 5.85$ (s, 1H, NH), 5.67 (ddd, $^3J \cong {}^3J = 6.8$, $^3J = 11.0$ Hz, 1H, C*H*CHCH$_2$CHO), 5.58 (ddd, $^3J \cong {}^3J = 6.0$, $^3J = 11.0$ Hz, 1H, CHC*H*CH$_2$CHO), 4.27 (ddd, $^3J = 3.8$, 8.8, 11.4 Hz, 1H, CHO), 3.74 (br dd, $^3J \cong {}^3J = 8.8$ Hz, 1H, CH$_2$C*H*CHO), 2.71 (ddd, $^2J = 15.0$ Hz, $^3J = 3.8$, 6.0 Hz, 1H, CH*H*CHO), 2.49 (ddd, $^2J = 15.0$, $^3J = 6.0$, 11.4 Hz, 1H, C*H*HCHO), 2.30–1.50 (m, 6H, C*H*$_2$C*H*$_2$C*H*$_2$CHNH); ^{13}C NMR (50 MHz): $\delta = 159.0$ (s, C=O), 131.6 (d, *C*HCHCH$_2$CHO), 124.2 (d, CH*C*HCH$_2$CHO), 84.0 (d, CHO), 59.3 (d, CHNH), 30.6 (t, CH$_2$CHO), 30.5 (t, *C*H$_2$CHNH), 25.0 (t, CH$_2$*C*H$_2$CH$_2$CHNH), 24.2 (t, *C*H$_2$CH$_2$CH$_2$CHNH); IR (film): $\tilde{\nu} = 3300-$ 3250 (br, NH), 2930 (m, C_{al}H), 2865 (m, C_{al}H), 1750 (vs, C=O), 1450 (w), 1400 (w), 1360 (w), 1240 (w, C-O-C), 1020 (m), 1000 (m), 955 (m), 745 cm^{-1} (m); MS (EI, 70eV): *m/z* (%): 86 (77) $[C_8H_{10}]^+$, 84 $(C_3H_2NO_2]^+$, 49 (39), 47 (32); elemental analysis calcd (%) for $C_9H_{13}NO_2$ (167.21): C 64.65, H 7.84, N 8.38; found: C 64.48, H 7.83, N 8.03.

4-{1-Chloro-2-[(*Z*)-hex-2-enyloxy]ethyl}-1,3-oxazolidin-2-one (32a): According to the general procedure (*Z*)-1-(azidocarbonyloxy)-4-[(*Z*)-hex-2-enyloxy]-but-2-ene (**31a**) (479 mg, 2.00 mmol) was treated with iron(II) chloride (25 mg, 0.20 mmol) and trimethyl silyl chloride (0.38 mL, 3.00 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) **32a** (393 mg, 79%) was obtained as a colorless oil. The product was a mixture of the (4*RS*,1′*RS*)- and the (4*RS*,1′*SR*)-isomer [*d.r.* = 53:47 (^{1}H NMR)]. $R_f = 0.19$ (P/TBME 20:80).

(4*RS*,1′*RS*)-*Isomer*: ^{1}H NMR (300 MHz): $\delta = 6.57$ (s, 1H, NH), 5.66–5.40 (m, 2H, C*H*C*H*CH$_2$CH$_2$), 4.50–4.16 (m, 3H, OC*H*$_2$C*H*NH), 4.15–3.90 (m, 3H, ClCHC*H*$_2$O, CHCl), 3.76–3.52 (m, 2H, OC*H*$_2$CHCH), 2.00 (dt, $^3J \cong {}^3J = 7.3$ Hz, 2H, C*H*$_2$CH$_2$CH$_3$), 1.36 (tq, $^3J \cong {}^3J = 7.3$Hz, 2H, C*H*$_2$CH$_3$), 0.87 (t, $^3J = 7.3$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): $\delta = 159.3$ (s, C=O), 134.7 (d, OCH$_2$CH*C*H), 124.9 (d, OCH$_2$*C*H), 71.4 (t, CHCl*C*H$_2$O), 67.9 (t, O*C*H$_2$CHCH), 66.9 (t, O*C*H$_2$CHNH), 59.6 (d, CHNH), 55.5 (d, CHCl), 29.5 (t, *C*H$_2$CH$_2$CH$_3$), 22.5 (t, *C*H$_2$CH$_3$), 13.6 (q, CH$_3$).

(4*RS*,1′*SR*)-*Isomer*: ^{1}H NMR (300 MHz): $\delta = 6.50$ (s, 1H, NH), 5.66–5.40 (m, 2H, C*H*C*H*CH$_2$CH$_2$), 4.50–4.16 (m, 3H, OC*H*$_2$C*H*NH), 4.15–3.90 (m,

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3H, ClCHCH_2O, CHCl), 3.76–3.52 (m, 2H, OCH_2CHCH), 2.00 (dt, $^3J \cong {}^3J = 7.3$ Hz, 2H, CH_2CH$_2$CH$_3$), 1.36 (tq, $^3J \cong {}^3J = 7.3$Hz, 2H, CH_2CH$_3$), 0.87 (t, $^3J = 7.3$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): $\delta = 159.4$ (s, C=O), 134.7 (d, OCH$_2$CH*C*H), 124.9 (d, OCH$_2$*C*H), 71.0 (t, CHClCH$_2$O), 67.5 (t, O*C*H$_2$CHCH), 66.9 (t, O*C*H$_2$CHNH), 60.4 (d, CHNH), 55.1 (d, CHCl), 29.5 (t, *C*H$_2$CH$_2$CH$_3$), 22.5 (t, *C*H$_2$CH$_3$), 13.6 (q, CH$_3$).

IR (film): $\tilde{\nu} = 3400-3200$ (br, NH), 2960 (m, C$_{al}$H), 2930 (m, C$_{al}$H), 2870 (m, C$_{al}$H), 1755 (vs, C=O), 1410 (m), 1240 (m, C-O-C), 1115 (m), 1040 (m), 935 cm^{-1} (w); MS (EI, 70eV): *m*/*z* (%): 178 (5) $[M - C_5H_9]^+$, 166 (28) $[M - C_6H_9]^+$, 114 (90) $[C_7H_{12}O]^+$, 86 (85) $[C_3H_4NO_2]^+$, 84 (40) $[C_3H_2NO_2]^+$, 82 (100), 55 (40) $[C_4H_9]^+$, 42 (24), 28 (25) $[CO]^+$; elemental analysis calcd (%) for $C_{11}H_{18}NO_3Cl$ (247.72): C 53.33, H 7.32, N 5.65; found: C 53.43, H 7.16, N 5.93.

4-{1-Chloro-2-[(*E*)-hex-2-enyloxy]ethyl}-1,3-oxazolidin-2-one (32b): According to the general procedure (*Z*)-1-(azidocarbonyloxy)-4-[(*E*)-hex-2-enyloxy]-but-2-ene (**31b**) (447 mg, 1.87 mmol) was treated with iron(II) chloride (25 mg, 0.20 mmol) and trimethyl silyl chloride (0.38 mL, 3.00 mmol) in ethanol (5 mL). After chromatographic purification (P/TBME 20:80) **32b** (369 mg, 80%) was obtained as a colorless oil. The product was a mixture of the (4*RS*,1′*RS*)- and (4*RS*,1′*SR*)-isomer [*d.r.* = 53:47 (^{1}H NMR)]. $R_f = 0.19$ (P/TBME 20:80).

(4*RS*,1′*RS*)-*Isomer*: ^{1}H NMR (300 MHz): $\delta = 6.98$ (s, 1H, NH), 5.64 (dt, $^3J = 6.5$, $^3J_{cis} = 15.2$ Hz, 1H, OCH$_2$CHC*H*), 5.42 (br dt, $^3J = 6.3$, $^3J_{cis} = 15.2$ Hz, 1H, C*H*CHCH$_2$CH$_2$), 4.45–4.03 (m, 3H, OCH_2*C*HNH), 4.00–3.92 (m, 1H, CHCl), 3.87 (d, $^3J = 6.8$ Hz, 2H, ClCHCH_2O), 3.70–3.45 (m, 2H, OCH_2CHCH), 1.94 (dt, $^3J \cong {}^3J = 7.2$ Hz, 2H, CH_2CH$_2$CH$_3$), 1.30 (tq, $^3J \cong {}^3J = 7.2$ Hz, 2H, CH_2CH$_3$), 0.80 (t, $^3J = 7.2$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): $\delta = 159.7$ (s, C=O), 135.5 (d, OCH$_2$CH*C*H), 125.2 (d, OCH$_2$*C*H), 72.0 (t, CHCl*C*H$_2$O), 70.6 (t, O*C*H$_2$CHCH), 67.5 (t, O*C*H$_2$CHNH), 60.1 (d, CHNH), 54.9 (d, CHCl), 34.0 (t, *C*H$_2$CH$_2$CH$_3$), 21.9 (t, *C*H$_2$CH$_3$), 13.4 (q, CH$_3$).

(4*RS*,1′*SR*)-*Isomer*: ^{1}H NMR (300 MHz): $\delta = 6.95$ (s, 1H, NH), 5.64 (dt, $^3J = 6.5$, $^3J_{cis} = 15.2$ Hz, 1H, OCH$_2$CHC*H*), 5.42 (br dt, $^3J = 6.3$, $^3J_{cis} = 15.2$ Hz, 1H, C*H*CHCH$_2$CH$_2$), 4.45–4.03 (m, 3H, OCH_2*C*HNH), 4.00–3.92 (m, 1H, CHCl), 3.87 (d, $^3J = 6.8$ Hz, 2H, ClCHCH_2O), 3.70–3.45 (m, 2H, OCH_2CHCH), 1.94 (dt, $^3J \cong {}^3J = 7.2$ Hz, 2H, CH_2CH$_2$CH$_3$), 1.30 (tq, $^3J \cong {}^3J = 7.2$ Hz, 2H, CH_2CH$_3$), 0.80 (t, $^3J = 7.2$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): $\delta = 159.6$ (s, C=O), 135.5 (d, OCH$_2$CH*C*H), 125.2 (d, OCH$_2$*C*H), 72.0 (t, CHCl*C*H$_2$O), 70.4 (t, O*C*H$_2$CHCH), 67.4 (t, O*C*H$_2$CHNH), 60.4 (d, CHNH), 54.7 (d, CHCl), 34.0 (t, *C*H$_2$CH$_2$CH$_3$), 21.9 (t, *C*H$_2$CH$_3$), 13.4 (q, CH$_3$).

IR (film): $\tilde{\nu} = 3400-3200$ (br, NH), 2960 (m, C$_{al}$H), 2930 (m, C$_{al}$H), 2870 (m, C$_{al}$H), 1755 (vs, C=O), 1410 (w), 1245 (m, C-O-C), 1120 (m), 1040 (m), 970 cm^{-1} (w); MS (EI, 70eV): *m*/*z* (%): 178 (2) $[M - C_5H_9]^+$, 166 (16) $[M - C_6H_9]^+$, 114 (100) $[C_7H_{12}O]^+$, 86 (85) $[C_3H_4NO_2]^+$, 84 (30) $[C_3H_2NO_2]^+$, 55 (44) $[C_4H_9]^+$, 41 (18) $[C_3H_5]^+$, 28 (27) $[CO]^+$; elemental analysis calcd (%) for $C_{11}H_{18}NO_3Cl$ (247.72): C 53.33, H 7.32, N 5.65; found: C 53.08, H 7.56, N 5.83.

4-(3-Butyltetrahydro-2-furyl)-1,3-oxazolidin-2-one (33): (4*RS*,1′*RS*)-4-(1-Chloro-2-[(*Z*)-hex-2-enyloxy]ethyl-1,3-oxazolidin-2-one (**32a**) (325 mg, 1.31 mmol) was dissolved in benzene (50 mL). The solution was degassed with a stream of argon for 15 min. After heating to reflux, a solution of tri-*n*-butyltinhydride (497 mg, 1.70 mmol) and *N*,*N*′-*bis*-azoisobutyronitrile (30 mg) in benzene (10 mL) was added via a syringe pump over a period of 3 h. The solution was refluxed for an additional hour. After cooling the solvent was removed in vacuo and the residue was purified by chromatography (P/TBME 20:80). **33** (257 mg, 92%) was obtained as a colorless oil. In an analogous fashion compound **32b** was converted to the bicyclic product **33** (85%). The product was a mixture of four diastereoisomers [*d.r.* = 23:25:27:25 (^{13}C NMR)]. $R_f = 0.08$ (P/TBME 20:80).

Isomer 1: ^{1}H NMR (300 MHz): $\delta = 6.60$ (s, 1H, NH), 4.38 (ddd, $^3J = 6.1$, $^3J \cong {}^3J = 7.5$ Hz, 1H C*H*NH), 4.05 (dd, $^2J = 7.6$, $^3J = 7.5$ Hz, 1H, OCH*H*CHNH), 4.00 (dd, $^2J = 7.5$, $^3J = 7.6$ Hz, 1H, OC*H*HCHNH), 3.82 (dd, $^2J = 8.6$, $^3J = 6.8$Hz, 1H, NHCHCHCHCH*H*O), 3.80 (dd, $^2J = 8.5$, $^3J = 6.2$ Hz, 1H, NHCHCHCHC*H*HO), 3.55 (dd, $^2J = 8.5$, $^3J = 6.2$ Hz, 1H, NHCHCHC*H*HO), 3.50 (dd, $^2J = 8.6$, $^3J = 6.4$ Hz, 1H, NHCHCHCHC*H*HO), 2.43 (dtt, $^3J = 6.8$ Hz, 1H, NHCHCHC*H*), 2.04–2.00 (m, 1H, NHCHC*H*CH$_2$O), 1.45–1.15 (m, 6H, CH$_3$CH_2CH_2CH_2), 0.88 (t, $^3J = 7.0$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): $\delta = 159.9$ (s, C=O), 72.5 (t, NHCHCHCH$_2$OCH$_2$), 68.8 (t, NHCHCH*C*H$_2$O), 68.1 (OCH$_2$CHNH), 51.6 (d, NHCH), 47.1 (t, NHCH*C*HCH), 40.9 (t, NHCHCH*C*H), 33.6 (t, CH$_3$CH$_2$CH$_2$*C*H$_2$), 30.6 (t, CH$_3$CH$_2$*C*H$_2$), 22.8 (t, CH$_3$*C*H$_2$), 13.9 (q, CH$_3$).

Isomer 2: ^{1}H NMR (300 MHz): $\delta = 6.68$ (s, 1H, NH), 4.43 (ddd, $^3J = 6.6$, $^3J \cong {}^3J = 8.0$ Hz, 1H, C*H*NH), 4.10–4.00 (m, 2H, OCH$_2$CHNH), 3.98 (dd, $^2J = 9.0$, $^3J = 6.5$Hz, 1H, NHCHCHCHCH*H*O), 3.95 (dd, $^2J = 8.6$, $^3J = 6.6$ Hz, 1H, NHCHCHCHC*H*HO), 3.58 (dd, $^2J = 9.0$, $^3J = 4.0$ Hz, 1H, NHCHCHC*H*HO), 3.32 (dd, $^2J = 8.6$, $^3J = 6.4$ Hz, 1H, NHCHCHCHC*H*HO), 2.35–2.20 (m, 1H, NHCHCHC*H*), 1.95–1.80 (m, 1H, NHCHC*H*CH$_2$O), 1.45–1.15 (m, 6H, CH$_3$CH_2CH_2CH_2), 0.88 (t, $^3J = 7.0$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): $\delta = 160.1$ (s, C=O), 73.9 (t, NHCHCHCH$_2$OCH$_2$), 69.2 (t, NHCHCH*C*H$_2$O), 68.5 (OCH$_2$CHNH), 51.6 (d, NHCH), 49.5 (t, NHCH*C*HCH), 41.7 (t, NHCHCH*C*H), 33.8 (t, CH$_3$CH$_2$CH$_2$*C*H$_2$), 30.3 (t, CH$_3$CH$_2$*C*H$_2$), 22.7 (t, CH$_3$*C*H$_2$), 13.9 (q, CH$_3$).

Isomer 3: ^{1}H NMR (300 MHz): $\delta = 7.08$ (s, 1H, NH), 4.04 (ddd, $^3J = 4.2$, $^3J \cong {}^3J = 6.8$ Hz, 1H, C*H*NH), 4.00–3.91 (m, 2H, OCH$_2$CHNH), 3.90–3.86 (m, 2H, NHCHCHCHCH$_2$O), 3.85 (dd, $^2J = 8.9$, $^3J = 6.8$ Hz, 1H, NHCHCHCH*H*O), 3.66 (dd, $^2J = 8.9$, $^3J = 6.4$ Hz, 1H, NHCHCHC*H*HO), 3.52 (dd, $^2J = 8.5$, $^3J = 7.0$ Hz, 1H, NHCHCHCHC*H*HO), 2.32 (dtt, $^3J = 7.0$ Hz, 1H, NHCHCHC*H*), 2.02–1.98 (m, 1H, NHCHC*H*CH$_2$O), 1.35–1.10 (m, 6H, CH$_3$CH_2CH_2CH_2), 0.86 (t, $^3J = 7.1$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): $\delta = 160.3$ (s, C=O), 73.8 (t, NHCHCHCH$_2$OCH$_2$), 69.3 (t, NHCHCH*C*H$_2$O), 68.7 (OCH$_2$CHNH), 54.8 (d, NHCH), 49.6 (t, NHCH*C*HCH), 41.4 (t, NHCHCH*C*H), 33.6 (t, CH$_3$CH$_2$CH$_2$*C*H$_2$), 30.6 (t, CH$_3$CH$_2$*C*H$_2$), 22.7 (t, CH$_3$*C*H$_2$), 13.8 (q, CH$_3$).

Isomer 4: ^{1}H NMR (300 MHz): $\delta = 6.92$ (s, 1H, NH), 4.04 (ddd, $^3J = 6.1$, $^3J \cong {}^3J = 3.2$ Hz, 1H, C*H*NH), 4.00–3.91 (m, 2H, OCH$_2$CHNH), 3.90 (m, 2H, NHCHCHCHCH$_2$O), 3.78 (dd, $^2J = 9.4$, $^3J = 6.8$ Hz, 1H, NHCHCHCH*H*O), 3.62 (dd, $^2J = 9.4$, $^3J = 4.5$ Hz, 1H, NHCHCHC*H*HO), 3.30 (dd, $^2J = 8.8$, $^3J = 6.6$ Hz, 1H, NHCHCHCHC*H*HO), 2.24–2.14 (m, 1H, NHCHCHC*H*), 1.89–1.75 (m, 1H, NHCHC*H*CH$_2$O), 1.35–1.10 (m, 6H, CH$_3$CH_2CH_2CH_2), 0.86 (t, $^3J = 7.1$ Hz, 3H, CH$_3$); ^{13}C NMR (75 MHz): $\delta = 160.1$ (s, C=O), 72.5 (t, NHCHCHCH$_2$OCH$_2$), 69.3 (t, NHCHCH*C*H$_2$O), 68.4 (OCH$_2$CHNH), 51.7 (d, NHCH), 47.4 (t, NHCH*C*HCH), 40.6 (t, NHCHCH*C*H), 33.7 (t, CH$_3$CH$_2$CH$_2$*C*H$_2$), 30.2 (t, CH$_3$CH$_2$*C*H$_2$), 22.7 (t, CH$_3$*C*H$_2$), 13.8 (q, CH$_3$).

IR (film): $\tilde{\nu} = 3400-3200$ (br, NH), 2955 (s, C$_{al}$H), 2930 (s, C$_{al}$H), 2860 (s, C$_{al}$H), 1760 (vs, C=O), 1415 (m), 1245 (m, C-O-C), 1025 (m), 730 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 116 (12), 86 (100) $[C_3H_4NO_2]^+$, 84 (26) $[C_3H_2NO_2]^+$, 68 (3) $[C_4H_4O]^+$; elemental analysis calcd (%) for $C_{11}H_{19}NO_3$ (213.28): C 61.95, H 8.98, N 6.57; found: C 61.88, H 8.99, N 6.69.

(*Z*)-4-(1-Chloro-1-phenylmethylidene)-5-cyclohexyl-1,3-oxazolidin-2-one (35a): According to the general procedure 1-azidocarbonyloxy-1-cyclohexyl-3-phenyl-2-propyne (**34a**) (283 mg, 1.00 mmol) was treated with iron(II) chloride (6 mg, 0.05 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). Compound **35a** (290 mg, 99%) was obtained as a colorless solid after work-up. It gradually decomposed in $CDCl_3$. M.p. 140–150 °C; ^{1}H NMR (400 MHz): $\delta = 7.91$ (s, 1H, NH), 7.39–7.30 (m, 5H, H$_{ar}$), 5.29 (br s, 1H, CHO), 1.90–0.89 (m, 11H, cyc-H); ^{13}C NMR (50 MHz): $\delta = 156.2$ (s, C=O), 135.3 (s, C$_{ar}$), 133.1 (d, C$_{ar}$H), 128.9 (d, C$_{ar}$H), 128.8 (s, CH*C*NH), 128.3 (d, C$_{ar}$H), 102.7 (s, C*C*Cl), 83.8 (d, CHO), 34.9 (d, cyc-CH), 28.9 (t, cyc-CH$_2$), 26.1 (t, cyc-CH$_2$), 25.7 (t, cyc-CH$_2$), 25.6 (t, cyc-CH$_2$), 23.9 (t, cyc-CH$_2$); IR (KBr): $\tilde{\nu} = 3300-3200$ (br, NH), 3120 (w, C$_{ar}$H), 2930 (m, C$_{al}$H), 2860 (m, C$_{al}$H), 1765 (vs, C=O), 1695 (m), 1445 (w), 1215 (m, C-O-C), 1075 (w), 1010 (w), 735 (w), 700 cm^{-1} (w); MS (EI, 70eV): *m*/*z* (%): 293 (12) $[M(^{37}Cl)]^+$, 291 (32) $[M(^{35}Cl)]^+$, 211 (34) $[M(^{37}Cl) - C_6H_{11}]^+$, 209 (100) $[M(^{35}Cl) - C_6H_{11}]^+$, 83 (38) $[C_6H_{11}]^+$, 77 (2) $[C_6H_5]^+$, 55 (52) $[C_4H_9]^+$, 41 (34) $[C_3H_5]^+$, 28 (75) $[CO]^+$; elemental analysis calcd (%) for $C_{16}H_{18}NO_2Cl$ (291.78): C 65.86, H 6.22, N 4.80; found: C 65.88, H 6.43, N 4.84.

(*Z*)-4-(1-Chloro-1-phenylmethylidene)-5-(2-phenylethyl)-1,3-oxazolidin-2-one (35b): According to the general procedure 3-azidocarbonyloxy-1,5-diphenyl-1-pentyne (**34b**) (611 mg, 2.00 mmol) was treated with iron(II) chloride (26 mg, 0.20 mmol) and trimethyl silyl chloride (0.38 mL, 3.00 mmol) in ethanol (5 mL). Compound **35b** (506 mg, 81%) was obtained as a colorless solid after work-up. It gradually decomposed in $CDCl_3$. M.p. 110–112 °C; ^{1}H NMR (400 MHz): $\delta = 7.85$ (s, 1H, NH), 7.40–6.60 (m, 10H, H$_{ar}$), 5.20 (t, $^3J = 6.3$ Hz, 1H, CHO), 2.48 (ddd, $^3J \cong {}^3J = 6.3$, $^3J = 13.1$ Hz, 2H, CH_2CH$_2$CHO), 1.52 (dd, $^3J = 6.3$, $^3J = 13.1$ Hz, 2H, CH$_2$CH_2CHO); ^{13}C NMR (50 MHz): $\delta = 156.2$ (s, C=O), 139.5 (s, C$_{ar}$), 134.9 (s, C$_{ar}$), 133.9 (d, C$_{ar}$H), 128.9 (d, C$_{ar}$H), 128.6 (s, HN*C*CCl), 128.5 (d,

$C_{ar}H$), 128.4 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 126.2 (d, $C_{ar}H$), 102.9 (s, CCl), 78.7 (d, C*H*CHO), 33.5 (t, *C*H_2CH_2CHO), 29.9 (t, CH_2*C*H_2CHO); IR (KBr): $\tilde{\nu}$ = 3200 – 3100 (br, NH), 3125 (w, $C_{ar}H$), 3065 (w, $C_{ar}H$), 3025 (w, $C_{ar}H$), 2965 (w, $C_{al}H$), 2930 (w, $C_{al}H$), 2870 (w, $C_{al}H$), 1770 (vs, C=O), 1670 (m), 1445 (m), 1375 (m), 1230 (m, C-O-C), 1030 (m), 1010 (w), 745 (m), 695 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 315 (11) $[M(^{37}Cl)]^+$, 313 (42) $[M(^{35}Cl)]^+$, 277 (11) $[M - Cl - H]^+$, 209 (23) $[M - C_8H_8]^+$, 174 (34), 115 (19), 105 (27) $[C_8H_9]^+$, 104 (63) $[C_8H_8]^+$, 91 (100) $[C_7H_7]^+$, 77 (11) $[C_6H_5]^+$; elemental analysis calcd (%) for $C_{18}H_{16}NO_2Cl$ (313.78): C 68.90, H 5.14, N 4.46; found: C 69.24, H 5.20, N 4.84.

(*Z*)-4-(1-Chloro-1-phenylmethylidene)-5-(cyclohex-3-enyl)-1,3-oxazolidin-2-one (35c): According to the general procedure 1-azidocarbonyloxy-1-(cyclohex-3-enyl)-3-phenyl-2-propyne (**34c**) (563 mg, 2.00 mmol) was treated with iron(II) chloride (26 mg, 0.20 mmol) and trimethyl silyl chloride (0.38 mL, 3.00 mmol) in ethanol (5 mL). **35c** (520 mg, 90%) was obtained as a colorless solid after work up. The product was a mixture of the (1′*RS*,5*RS*)- and the (1′*RS*,5*SR*)-isomer [*d.r.* = 57:43 (^{1}H NMR)]. It gradually decomposed in $CDCl_3$. M.p. 140 – 144 °C.

(1′*RS*,5*RS*)-*Isomer*: ^{1}H NMR (200 MHz): δ = 7.90 (br s, 1H, NH), 7.30 – 7.10 (m, 5H, H_{ar}), 5.50 – 5.44 (m, 2H, *HC*=C*H*), 5.38 (d, ^3J = 4.0 Hz, 1H, CHO), 2.30 – 1.20 (m, 7H, cyc-H); ^{13}C NMR (50 MHz): δ = signal for C=O not observed, 135.1 (s, C_{ar}), 132.8 (d, $C_{ar}H$), 129.0 (d, $C_{ar}H$), 128.9 (s, HN*C*CCl), 128.2 (d, $C_{ar}H$), 126.6 (d, CH=*C*HCH$_2$CH), 124.9 (d, *C*H=CHCH$_2$CH), 102.8 (s, CCl), 83.3 (d, CHO), 35.9 (d, C*H*CHO), 27.5 (t, CH_2), 25.1 (t, CH_2), 23.0 (t, CH_2).

(1′*RS*,5*SR*)-*Isomer*: ^{1}H NMR (200 MHz): δ = 7.90 (br s, 1H, NH), 7.30 – 7.10 (m, 5H, H_{ar}), 5.50 – 5.44 (m, 2H, *HC*=C*H*), 5.37 (d, ^3J = 5.3 Hz, 1H, CHO), 2.30 – 1.20 (m, 7H, cyc-H); ^{13}C NMR (50 MHz): δ = signal for C=O not observed, 135.2 (s, C_{ar}), 133.0 (d, $C_{ar}H$), 129.0 (d, $C_{ar}H$), 128.9 (s, HN*C*CCl), 128.2 (d, $C_{ar}H$), 126.6 (d, CH=*C*HCH$_2$CH), 125.5 (d, *C*H=CHCH$_2$CH), 102.8 (s, CCl), 82.8 (d, CHO), 36.3 (d, C*H*CHO), 27.5 (t, CH_2), 24.9 (t, CH_2), 20.5 (t, CH_2).

IR (KBr): $\tilde{\nu}$ = 3300 – 3200 (br, NH), 3125 (w, $C_{ar}H$), 2930 (m, $C_{al}H$), 2840 (w $C_{al}H$), 1770 (vs, C=O), 1695 (m), 1680 (m, C=C), 1445 (w), 1215 (m, C-O-C), 1055 (w), 980 (w), 760 (m), 700 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 291 (5) $[M(^{37}Cl)]^+$, 289 (20) $[M(^{35}Cl)]^+$, 210 (50) $[M(^{37}Cl) - C_6H_7]^+$, 164 (39) $[M - C_7H_6Cl]^+$, 81 (100) $[C_6H_9]^+$, 80 (83) $[C_6H_8]^+$, 79 (39) $[C_6H_7]^+$; elemental analysis calcd (%) for $C_{16}H_{16}NO_2Cl$ (289.76): C 66.32, H 5.57, N 4.83; found: C 66.21, H 5.46, N 5.03.

(*Z*)-4-(1-Chloro-1-phenylmethylidene)-5-propyl-1,3-oxazolidin-2-one (35d): According to the general procedure 3-azidocarbonyloxy-1-phenyl-1-hexyne (**34d**) (243 mg, 1.00 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL).Compound **35d** (249 mg, 99%) was obtained as a colorless solid after work-up. It gradually decomposed in $CDCl_3$. M.p. 124 – 125 °C; ^{1}H NMR (300 MHz): δ = 7.40 (s, 1H, NH), 7.40 – 7.25 (m, 5H, H_{ar}), 5.45 (dd, ^3J = 3.2, ^3J = 6.4 Hz, 1H, CHO), 1.44 – 1.25 (m, 4H, $CH_3CH_2CH_2$), 0.74 (t, ^3J = 7.0 Hz, 3H, CH_3); ^{13}C NMR (50 MHz): δ = signal for C=O not observed, 135.1 (s, C_{ar}), 134.1 (d, $C_{ar}H$), 129.0 (s, HN*C*CCl), 128.9 (d, $C_{ar}H$), 128.3 (d, $C_{ar}H$), 102.7 (s, CCl), 79.7 (d, CHO), 34.2 (t, $CH_3CH_2CH_2$), 17.0 (t, CH_3CH_2), 13.3 (q, CH_3); IR (KBr): $\tilde{\nu}$ = 3300 – 3200 (br, NH), 3115 (w, $C_{ar}H$), 2955 (w, $C_{al}H$), 2930 (w, $C_{al}H$), 2875 (w, $C_{al}H$), 1760 (vs, C=O), 1680 (m, C=C), 1445 (m), 1375 (m), 1220 (m, C-O-C), 1065 (m), 1035 (m), 765 (m), 695 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 253 (27) $[M(^{37}Cl)]^+$, 251 (100) $[M(^{35}Cl)]^+$, 208 (32) $[M(^{35}Cl) - C_3H_7]^+$, 165 (50); elemental analysis calcd (%) for $C_{13}H_{14}NO_2Cl$ (251.71): C 62.03, H 5.61, N 5.56; found: C 62.13, H 5.64, N 5.89.

(*Z*)-4-(1-Chloro-1-phenylmethylidene)-1,3-oxazolidin-2-one (35e): According to the general procedure 3-azidocarbonyloxy-1-phenyl-1-propyne (**34e**) (201 mg, 1.00 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). Compound **35e** (211 mg, 99%) was obtained as a colorless solid after work-up. It gradually decomposed in $CDCl_3$. M.p. 110 – 115 °C; ^{1}H NMR (300 MHz): δ = 8.35 (br s, 1H, NH), 7.75 – 7.40 (m, 5H, H_{ar}), 5.35 (s, OCH_2); ^{13}C NMR (75 MHz): δ = 156.4 (s, C=O), 134.7 (s, C_{ar}), 130.4 (d, $C_{ar}H$), 128.8 (d, $C_{ar}H$), 128.4 (d, $C_{ar}H$), 127.0 (s, HN*C*CCl), 103.5 (s, CCl), 68.1 (t, OCH_2); IR (KBr): ν = 3300 – 3200 (br, NH), 3120 (w, $C_{ar}H$), 1755 (vs, C=O), 1680 (w, C=C), 1660 (m, C=C), 1385 (m), 1225 (m, C-O-C), 1040 (m), 1030 (m), 765 (m), 725 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 209 (100) $[M]^+$, 138 (41), 130 (78) $[M - Cl - CO_2]^+$, 103 (74), 89 (29) $[C_7H_5]^+$, 77 (26) $[C_6H_5]^+$; elemental analysis calcd (%) for $C_{10}H_8NO_2Cl$ (209.63): C 57.30, H 3.85, N 6.68; found: C 57.30, H 4.05, N 6.46.

3-Azidocarbonyloxy-1-phenyl-non-4-yne (36): As described for the preparation of azide **24** 1-phenyl-non-4-yn-3-ol (2.16 g, 10.0 mmol) was subjected to azidocarbonylation. After chromatographic purification (P/TBME 60:40) compound **36** (2.59 g, 91%) was obtained as a yellow liquid. R_f = 0.64 (P/TBME 60:40); ^{1}H NMR (200 MHz): δ = 7.25 – 7.00 (m, 5H, H_{ar}), 5.18 (tt, ^3J = 6.5, ^5J = 2.0 Hz, 1H, OCH), 2.68 (t, ^3J = 7.8 Hz, 2H, PhCH_2CH_2), 2.11 (dt, ^3J = 6.9, ^5J = 2.0 Hz, 2H, OCHCCCH_2), 2.06 – 1.92 (m, 2H, $PhCH_2CH_2$), 1.48 – 1.20 (m, 4H, $CH_2CH_2CH_3$), 0.80 (t, ^3J = 7.9 Hz, 3H, CH_3); ^{13}C NMR (50 MHz): δ = 156.7 (s, C=O), 140.4 (s, C_{ar}), 128.5 (d, $C_{ar}H$), 128.3 (d, $C_{ar}H$), 126.2 (d, $C_{ar}H$), 88.5 (s, OCHC*C*CH_2), 75.6 (s, OCH*C*CCH_2), 68.8 (d, OCH), 36.5 (t, PhCH_2CH_2), 31.1 (t, PhCH_2), 30.4 (t, $CH_2CH_2CH_2CH_3$), 21.9 (t, $CH_2CH_2CH_3$), 18.3 (t, CH_2CH_3), 13.5 (q, CH_3); IR (film): $\tilde{\nu}$ = 3030 (w, $C_{ar}H$), 2960 (m, $C_{al}H$), 2930 (m, $C_{al}H$), 2190 (s, N_3), 2135 (s, N_3), 1735 (vs, C=O), 1235 (vs, C-O-C), 1010 (w), 750 (w), 700 cm^{-1} (w); MS (EI, 70eV): *m*/*z* (%): 198 (6) $[M - HOCN_3]^+$, 104 (14) $[C_8H_8]^+$, 91 (51) $[C_7H_7]^+$, 28 (100) $[N_2, CO]^+$; elemental analysis calcd (%) for $C_{16}H_{19}N_3O_2$ (285.34): C 67.35, H 6.71, N 14.73; found: C 67.16, H 6.85, N 14.35.

(*Z*)-4-(1-Chloro-1-pentylidene)-5-(2-phenylethyl)-1,3-oxazolidin-2-one (37): According to the general procedure 3-azidocarbonyloxy-1-phenyl-4-nonyne (**36**) (285 mg, 1.00 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). Compound **37** (265 mg, 95%) was obtained as a yellow oil. It considerably decomposed in $CDCl_3$. ^{1}H NMR (200 MHz): δ = 8.60 (s, 1H, NH), 7.20 – 6.90 (m, 5H, H_{ar}), 4.92 (t, ^3J = 5.7 Hz, 1H, CHO), 2.85 – 2.50 (m, 2H, CH_2CH_2CHO), 1.92 (t, ^3J = 7.2 Hz, 4H, CH_2CH_2CHO, $ClCCH_2$), 1.55 – 1.00 (m, 4H, $CH_3CH_2CH_2$), 0.75 (t, ^3J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (50 MHz): δ = 156.9 (s, C=O), 139.9 (s, C_{ar}), 131.6 (s, HN*C*CCl), 128.4 (d, $C_{ar}H$), 126.2 (d, $C_{ar}H$), 125.9 (d, $C_{ar}H$), 105.9 (s, CCl), 77.6 (d, CHO), 36.3 (t, CH_2), 32.4 (t, PhCH_2CH_2), 29.9 (t, PhCH_2CH_2), 29.4 (t, CH_2), 21.7 (t, CH_2), 13.6 (q, CH_3); IR (film): $\tilde{\nu}$ = 3200 – 3100 (br, NH), 3060 (w, $C_{ar}H$), 3030 (w, $C_{ar}H$), 2960 (w, $C_{al}H$), 2930 (w, $C_{al}H$), 2870 (w, $C_{al}H$), 1760 (vs, C=O), 1600 (m), 1455 (m), 1400 (m), 1055 (m), 1010 (w), 700 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 293 (< 1) $[M]^+$, 258 (1) $[M - Cl]^+$, 230 (9) $[M - Cl - CHCH_3]^+$, 215 (10) $[M - Cl - CH_2CH_2CH_3]^+$, 207 (96), 133 (87) $[C_9H_9O]^+$, 105 (87) $[C_8H_9]^+$, 91 (100) $[C_7H_7]^+$, 55 (15) $[C_4H_7]^+$, 43 (40) $[C_3H_7]^+$; HRMS calcd for $C_{16}H_{20}NO_2{}^{35}Cl$: 293.1183; found: 293.1187.

(*Z*)-5-Cyclohexyl-4-[1-(2,2-dimethylpropylidene)]-5-ethoxy-1,3-oxazolidin-2-one (39a): According to the general procedure 5-azidocarbonyloxy-7-cyclohexyl-2,2-dimethyl-3-heptyne (**38a**) (263 mg, 1.00 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). Compound **39a** (261 mg, 93%) was obtained as a colorless solid. It gradually decomposed in $CDCl_3$. M.p. 180 – 185 °C; ^{1}H NMR (300 MHz): δ = 7.85 (br s, 1H, NH), 4.48 [s, 1H, *H*CC$(CH_3)_3$], 3.45 (dq, ^3J = 7.2, ^6J = 1.5 Hz, 2H, CH_3CH_2), 2.05 – 1.00 [m, 23H, cyc-H, $C(CH_3)_3$, CH_2CH_3]; ^{13}C NMR (75 MHz): δ = 156.0 (s, C=O), 130.1 (s, OOC*C*NH), 112.0 [d, H*C*C$(CH_3)_3$], 111.9 (s, OO*C*CNH), 58.5 (t, CH_3CH_2), 47.0 (d, cyc-CH), 31.7 [s, *C*$(CH_3)_3$], 30.3 [q, C(*C*$H_3)_3$], 26.2 (t, cyc-CH_2), 26.0 (t, cyc-CH_2), 25.9 (t, cyc-CH_2), 25.2 (t, cyc-CH_2), 14.9 (q, *C*H_3CH_2); IR (KBr): $\tilde{\nu}$ = 3200 – 3100 (br, NH), 2975 (w, $C_{al}H$), 2930 (m, $C_{al}H$), 2880 (w, $C_{al}H$), 1755 (vs, C=O), 1695 (m), 1370 (w), 1320 (w), 1230 (w, C-O-C), 1200 (w), 1165 (w), 905 (w), 690 cm^{-1} (w); MS (EI, 70eV): *m*/*z* (%): 237 (4) $[M - C_2H_5OH]^+$, 208 (66), 198 (43) $[M - C_6H_{11}]^+$, 152 (47), 87 (36), 83 (57) $[C_6H_{11}]^+$, 82 (53) $[C_6H_{10}]^+$, 69 (47), 57 (46) $[C_4H_9]^+$, 55 (58) $[C_4H_7]^+$, 41 (100) $[C_3H_5]^+$; elemental analysis calcd (%) for $C_{16}H_{27}NO_3$ (281.39): C 68.30, H 9.67, N 4.98; found: C 68.57, H 9.42, N 5.10.

(*Z*)-4-[1-(2,2-Dimethylpropylidene)]-5-ethoxy-5-(2-phenylethyl)-1,3-oxazolidin-2-one (39b): According to the general procedure 5-azidocarbonyloxy-7-phenyl-2,2-dimethyl-3-heptyne (**38b**) (285 mg, 1.00 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in ethanol (5 mL). Compound **39b** (285 mg, 95%) was obtained as a colorless solid. It gradually decomposed in $CDCl_3$. M.p. 153 – 158 °C; ^{1}H NMR (200 MHz): δ = 8.25 (br s, 1H, NH), 7.30 – 7.00 (m, 5H, H_{ar}), 4.51 [s, 1H, *H*CC$(CH_3)_3$], 3.46 (dq, ^3J = 7.0, ^5J = 1.2 Hz, 2H, CH_3CH_2), 2.70 (ddd, ^2J = 13.6, ^3J = 5.0, ^3J = 13.6 Hz, 1H, CCH*H*CH_2COO), 2.68 (ddd, ^2J = 13.6, ^3J = 5.0, ^3J = 13.6 Hz, 1H, C*H*HCH_2COO), 2.16 (ddd, ^2J = 11.8, ^3J = 5.0, ^3J = 13.6 Hz, 1H, CH_2CH*H*COO), 1.97 (ddd, ^2J = 11.8, ^3J = 5.0, ^3J = 13.6 Hz, 1H, CH_2C*H*HCOO), 1.10 (t, ^3J = 7.0 Hz, 3H, CH_3CH_2), 1.08 [s, 9H, $(CH_3)_3$];

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^{13}C NMR (50 MHz): $\delta = 155.6$ (s, C=O), 141.0 (s, C_{ar}), 130.5 (s, OOC*C*NH), 128.4 (d, $C_{ar}H$), 128.3 (d, $C_{ar}H$), 125.9 (d, $C_{ar}H$), 112.5 [d, H*C*C$(CH_3)_3$], 109.8 (s, OO*C*CNH), 58.7 (t, CH_3CH_2O), 41.7 (t, CH_2CH_2COO), 31.8 [s, *C*$(CH_3)_3$], 30.3 [q, C$(CH_3)_3$)], 29.0 (t, CH_2CH_2COO), 14.9 (q, CH_3CH_2); IR (KBr): $\tilde{\nu} = 3200-3100$ (br, NH), 3100 (w, $C_{ar}H$), 3025 (w, $C_{ar}H$), 2965 (w, $C_{al}H$), 2935 (w, $C_{al}H$), 2870 (w, $C_{al}H$), 1755 (vs, C=O), 1695 (m), 1455 (w), 1330 (m), 1205 (w, C-O-C), 995 (m), 885 (m), 690 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 303 (<1) $[M]^+$, 258 (2) $[M - OCH_2CH_3]^+$, 199 (97) $[M - OCH_2CH_3 - HC(CH_3)_3]^+$, 168 (79), 105 (26) $[C_8H_9]^+$, 91 (100) $[C_7H_7]^+$, 57 (22) $[C(CH_3)_3]^+$; elemental analysis calcd (%) for $C_{18}H_{25}NO_3$ (303.40): C 71.26, H 8.31, N 4.83; found: C 71.29, H 8.11, N 4.83.

(*Z*)-4-[1-(2,2-Dimethylpropylidene)]-5-(1-methylethoxy)-5-(2-phenylethyl)-1,3-oxazolidin-2-one (39c): According to the general procedure 5-azidocarbonyloxy-7-phenyl-2,2-dimethyl-3-heptyne (**38b**) (285 mg, 1.00 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in isopropanol (5 mL). Compound **39c** (315 mg, 99%) was obtained as a colorless solid. It gradually decomposed in $CDCl_3$. M.p. 93–95 °C; ^{1}H NMR (200 MHz): $\delta =$ 7.98 (br s, 1H, NH), 7.50–7.20 (m, 5H, H_{ar}), 4.70 [s, 1H, H*C*C$(CH_3)_3$], 3.98 (sept, $^3J = 6.1$ Hz, 1H, C*H*$(CH_3)_2$), 2.85 (ddd, $^2J = 13.9$, $^3J = 5.5$, $^3J =$ 13.9 Hz, 1H, CCH*H*CH_2COO), 2.78 (ddd, $^2J = 13.9$, $^3J = 5.5$, $^3J = 13.9$ Hz, 1H, C*H*HCH_2COO), 2.33 (ddd, $^2J = 11.5$, $^3J = 5.5$, $^3J = 13.9$ Hz, 1H, CH_2CH*H*COO), 2.10 (ddd, $^2J = 11.5$, $^3J = 5.5$, $^3J = 13.9$ Hz, 1H, CH_2C*H*HCOO), 1.32 (d, $^3J = 6.1$ Hz, 6H, CH(CH_3)$_2$), 1.25 [s, 9H, $(CH_3)_3$]; ^{13}C NMR (50 MHz): $\delta = 155.5$ (s, C=O), 141.1 (s, C_{ar}), 131.4 (s, OOC*C*NH), 128.4 (d, $C_{ar}H$), 128.3 (d, $C_{ar}H$), 125.9 (d, $C_{ar}H$), 112.5 [d, H*C*C$(CH_3)_3$], 110.5 (s, OO*C*CNH), 68.2 (d, *C*H$(CH_3)_2$), 42.2 (t, CH_2CH_2COO), 31.9 [s, *C*$(CH_3)_3$], 30.3 [q, C$(CH_3)_3$], 29.0 (t, CH_2CH_2COO), 24.1 [q, CH(*C*H_3)$_2$]; IR (KBr): $\tilde{\nu} = 3200-3100$ (br, NH), 3095 (w, $C_{ar}H$), 3060 (w, $C_{ar}H$), 2970 (m, $C_{al}H$), 2870 (w, $C_{al}H$), 1755 (vs, C=O), 1695 (vs), 1600 (s), 1500 (w), 1455 (m), 1370 (m), 1310 (m), 1230 (m), 1210 (m), 1160 (m), 1000 (m), 960 (m), 895 (m), 750 (m), 700 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 273 (1), 258 (6) $[M - OC_3H_7]$, 216 (48), 171 (31), 140 (42), 127 (36), 105 (28) $[C_8H_9]^+$, 91 (100) $[C_7H_7]^+$, 57 (30) $[C_4H_9]^+$, 43 (80) $[C_3H_7]^+$; elemental analysis calcd (%) for $C_{19}H_{27}NO_3$ (317.43): C 71.89, H 8.57, N 4.41; found: C 72.28, H 8.35, N 4.63.

4-[1-Chloro-1-(2,2-dimethylpropyl)]-5-cyclohexyl-1,3-oxazolin-2-one (41a): According to the general procedure 1-azidocarbonyloxy-1-cyclohexyl-4,4-dimethyl-2-pentyne (**38a**) (270 mg, 1.02 mmol) was treated with iron(II) chloride (13 mg, 0.10 mmol) and trimethyl silyl chloride (0.19 mL, 1.50 mmol) in acetonitrile (5 mL). A yellow oil was obtained (246 mg). *n*-Pentane (5 mL) was added and the supernatant solution was collected. After removal of the solvent in vacuo 1-azidocarbonyloxy-1-cyclohexyl-4,4-dimethyl-2-pentyne (**38b**) (200 mg, 74%) was isolated. The residue which was not soluble in *n*-pentane was identified as 4-[1-chloro-1-(2,2,-dimethylpropyl)]-5-cyclohexyl-1,3-oxazolin-2-one (**41b**) (44 mg, 16%). The compound quickly decomposed in $CDCl_3$. ^{1}H NMR (300 MHz): $\delta =$ 9.30 (s, 1H, NH), 4.50 (br s, 1H, CHCl), 1.80–0.80 [m, 20H, C$(CH_3)_3$, cyc-H]; ^{13}C NMR (75 MHz): $\delta = 156.3$ (s, C=O), 142.4 (s, OCCCCHCl), 117.5 (s, HNCCHCl), 62.6 (d, CHCl), 41.9 (d, cyc-CH), 30.7 (t, cyc-CH_2), 30.6 (t, cyc-CH_2), 30.4 [s, *C*$(CH_3)_3$], 26.9 [q, C$(CH_3)_3$], 26.0 (t, cyc-CH_2), 25.9 (t, cyc-CH_2), 25.4 (t, cyc-CH_2); IR (film): $\tilde{\nu} = 3200-3000$ (br, NH), 2930 (m, $C_{al}H$), 2860 (m, $C_{al}H$), 1760 (vs, C=O), 1680 (w, C=C), 1450 (w), 1235 (m, C-O-C), 970 (m), 760 cm^{-1} (m); MS (EI, 70eV): *m*/*z* (%): 271 (7) $[M]^+$, 236 (13) $[M - Cl]^+$, 235 (20) $[M - Cl - H]^+$, 220 (18) $[M - Cl - H\text{-}CH_3]^+$, 215 (38) $[M - Cl - H - 2 \times CH_3]$, 83 (74) $[C_6H_{11}, C_3HNO_2]^+$, 81 (11) $[C_6H_9]^+$, 57 (100) $[C_4H_9]^+$, 41 (44) $[C_3H_5]^+$; HRMS calcd for $C_{14}H_{22}NO_2{}^{35}Cl$: 271.1339; found: 271.1334.

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[15] Crystal data of compound **19** ($C_{11}H_{12}ClNO_2$, $M_r = 225.67$): crystal size $0.75 \times 0.17 \times 0.17$ mm^3, orthorhombic, space group *Iba*2, $a =$ 1104.78(12), $b = 2802.4(3)$, $c = 726.93(7)$ pm, $U = 2250.6(4)$ Å^3, $\rho_{calcd} = 1.332$ g cm^{-3} for $Z = 8$, $F(000) = 944$, $\mu = 0.319$ mm^{-1}, Stoe IPDS diffractometer, $\lambda = 0.71073$ Å, ω scan, 6369 reflections ($-h$, $+k$, $\pm l$), $\Theta_{max} = 26.1°$, 2182 independent and 1556 observed reflections [$F \geq 4\sigma(F)$], 184 refined parameters, $R = 0.0322$, $wR2 = 0.0785$, residual electron density 0.199 e Å^{-3}, direct methods, hydrogen atoms calculated.[32]

[16] Crystal data of compound **21** ($C_7H_{10}ClNO_2$, $M_r = 175.61$): crystal size $0.30 \times 0.18 \times 0.03$ mm³, monoclinic, space group $P2(1)/c$, $a = 533.39(8)$, $b = 1246.01(17)$, $c = 1182.03(17)$ pm, $U = 783.80(19)$ Å³, $\rho_{calcd} = 1.488$ g cm^{-3} for $Z = 4$, $F(000) = 368$, $\mu = 0.433$ mm^{-1}, Stoe IPDS diffractometer, $\lambda = 0.71073$ Å, ω scan, 4857 reflections ($-h$, $+k$, $\pm l$), $\Theta_{max} = 25.9°$, 1500 independent and 990 observed reflections [$F \geq 4\sigma(F)$], 140 refined parameters, $R = 0.0345$, $wR2 = 0.0719$, residual electron density 0.225 e Å^{-3}, direct methods, hydrogen atoms calculated.[32]

[17] Crystal data of compound **25** ($C_9H_{12}ClNO_2$, $M_r = 201.65$): crystal size $0.45 \times 0.45 \times 0.15$ mm³, monoclinic, space group $P2(1)/n$, $a = 992.46(5)$, $b = 689.08(3)$, $c = 1419.18(10)$ pm, $U = 965.77(9)$ Å³, $\rho_{calcd} = 1.387$ g cm^{-3} for $Z = 4$, $F(000) = 424$, $\mu = 3.246$ mm^{-1}, Enraf Nonius CAD4 diffractometer, $\lambda = 1.54178$ Å, ω scan, 1924 reflections ($-h$, $+k$, $\pm l$), $\Theta_{max} = 70.3°$, 1817 independent and 1650 observed reflections [$F \geq 4\sigma(F)$], 166 refined parameters, $R = 0.0599$, $wR2 = 0.1780$, residual electron density 0.383 e Å^{-3}, direct methods, hydrogen atoms calculated.[32]

[18] Crystal data of compound **26** ($C_9H_{12}ClNO_2$, $M_r = 201.65$): crystal size $0.45 \times 0.40 \times 0.18$ mm³, monoclinic, space group $P2(1)/n$, $a = 1196.78(13)$, $b = 629.49(3)$, $c = 1374.72(10)$ pm, $U = 950.75(16)$ Å³, $\rho_{calcd} = 1.409$ g cm^{-3} for $Z = 4$, $F(000) = 424$, $\mu = 3.298$ mm^{-1}, Enraf Nonius CAD4 diffractometer, $\lambda = 1.54178$ Å, ω scan, 1255 reflections ($-h$, $+k$, $\pm l$), $\Theta_{max} = 55.0°$, 1197 independent and 1050 observed reflections [$F \geq 4\sigma(F)$], 122 refined parameters, $R = 0.0617$, $wR2 = 0.1855$, residual electron density 0.295 e Å^{-3}, direct methods, hydrogen atoms calculated.[32]

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[22] Crystal data of compound **33** ($C_{11}H_{19}NO_3$, $M_r = 213.27$): crystal size $0.40 \times 0.30 \times 0.20$ mm³, triclinic, space group $P\bar{1}$, $a = 561.4(1)$, $b = 705.8(1)$, $c = 1590.2(1)$ pm, $U = 585.1(1)$ Å³, $D_c = 1.211$ g cm^{-3} for $Z = 2$, $F(000) = 232$, $\mu = 0.713$ mm^{-1}, Enraf Nonius CAD4 diffractometer, $\lambda = 1.54184$ Å, ω scan, 1810 reflections ($-h$, $+k$, $\pm l$), $\Theta_{max} = 59.9°$, 1738 independent and 1078 observed reflections [$F \geq 4\sigma(F)$], 176 refined parameters, $R = 0.0688$, $wR2 = 0.1971$, residual electron density 0.252 e Å^{-3}, direct methods, hydrogen atoms calculated. In the crystal a mixture of two diastereoisomers was present.[32]

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[26] Crystal data of compound **35d** ($C_{13}H_{14}ClNO_2$, $M_r = 251.70$): crystal size $1.20 \times 0.60 \times 0.24$ mm³, monoclinic, space group $P2(1)/n$, $a = 691.44(6)$, $b = 935.2(3)$, $c = 1994.86(11)$ pm, $U = 1272.6(4)$ Å³, $\rho_{calcd} = 1.314$ g cm^{-3} for $Z = 4$, $F(000) = 528$, $\mu = 2.577$ mm^{-1}, Enraf Nonius CAD4 diffractometer, $\lambda = 1.54178$ Å, ω scan, 4955 reflections ($-h$, $+k$, $\pm l$), $\Theta_{max} = 69.9°$, 2409 independent and 1464 observed reflections [$F \geq 4\sigma(F)$], 191 refined parameters, $R = 0.0593$, $wR2 = 0.1735$, residual electron density 0.339 e Å^{-3}, direct methods, hydrogen atoms calculated.[32]

[27] Crystal data of compound **39a** ($C_{16}H_{27}NO_3$, $M_r = 281.39$): crystal size $0.52 \times 0.24 \times 0.12$ mm³, triclinic, space group $P\bar{1}$, $a = 935.39(8)$, $b = 943.38(6)$, $c = 1024.06(5)$ pm, $U = 813.61(10)$ Å³, $\rho_{calcd} = 1.149$ g cm^{-3} for $Z = 2$, $F(000) = 308$, $\mu = 0.625$ mm^{-1}, Enraf Nonius CAD4 diffractometer, $\lambda = 1.54178$ Å, ω scan, 3263 reflections ($-h$, $+k$, $\pm l$), $\Theta_{max} = 69.9°$, 3076 independent and 2516 observed reflections [$F \geq 4\sigma(F)$], 289 refined parameters, $R = 0.0571$, $wR2 = 0.1613$, residual electron density 0.259 e Å^{-3}, direct methods, hydrogen atoms calculated.[32]

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[32] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-153441 (**19**), -153442 (**21**), -153443 (**25**), -153444 (**26**), -153445 (**33**), -153446 (**35d**), -153447 (**39a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 EZ1, UK (fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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