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# Cyclization of Trichloroacetimidates by Olefin Aminopalladation β-Heteroatom Elimination

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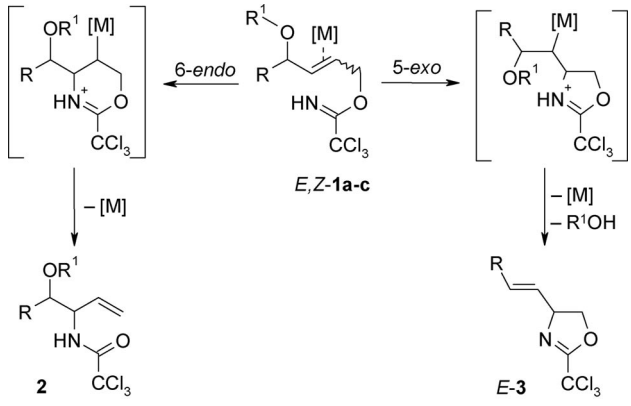
The cyclization of δ-acetoxy-*O*-allyl- and ε-acetoxy-*O*-homoallyl-trichloroacetimidates to 4-vinyloxazolines and a 4-vinyldihydrooxazine has been efficiently achieved by olefin aminopalladation–β-heteroatom elimination. (*Z*)-Allylic imidates bearing a secondary δ-acetoxy group underwent $Pd^{II}$-catalysed cyclization to give the *E* isomers of 4-vinyloxazolines selectively and gave no Overman rearrangement products. Using a chiral substrate, it has been demonstrated that cyclization to 4-vinyloxazolines occurs with high chirality transfer. Stereoselective *E* isomer formation and chirality transfer provided a basis from which to discuss the possible reaction mechanism.


## Introduction

The transition-metal-catalysed formation, particularly with palladium, of the $C_{sp^3}$–N bond by amination of olefins has emerged as a powerful tool in organic synthesis. Distinguished methods are inter- and intramolecular $Pd^{II}$-catalysed oxidative amination using co-oxidants to regenerate the catalyst[1] as well as oxyamination[2] and deamination,[3] which are believed to proceed by a co-oxidant promoted Pd(II/IV) catalytic cycle. Other notable intramolecular reactions of this type are $Pd^{II}$-catalysed olefin hydroamination[4] terminated by the protolysis of the C–Pd bond and olefin haloamination[5] involving oxidative palladium–halide exchange in an alkylpalladium intermediate. An alternative way to regenerate the metal in the oxidation state required to maintain the catalytic cycle is β-heteroatom elimination from the alkylpalladium intermediate. A well-known example of this approach is the catalytic Overman rearrangement in which aminopalladation of the double bond is followed by elimination of the protonated β-imidate.[6] A few other related cyclization reactions of unsaturated carbamates by aminopalladation–deoxypalladation have also been reported.[7]

Recently we have demonstrated that metal-catalysed Overman rearrangement of (*E*)-allylic imidates (*E*)-**1** (R = Me, $R^1$ = Me, TBS) bearing an oxy substituent at the δ position gives 4-vinyloxazolines **3** (R = Me) as byproducts of the amides **2** (Scheme 1).[8] 4-Vinyloxazoline **3** formation was proposed to be a result of a competitive 5-*exo* aminometallation–deoxymetallation sequence in analogy to the CIR (cyclization-induced rearrangement) mechanism of the Overman rearrangement. The reaction is similar to the cyclization of δ-acetoxy-*O*-allyl-*N*-tosylcarbamates.[7a,7b,7f] However, it provides products that can be transformed into amino alcohol derivatives under relatively mild reaction conditions.[9a–9d]




Scheme 1. Metal-catalysed 6-*endo* and 5-*exo* aminometallation with subsequent deoxymetallation.

The high synthetic value of 4-vinyloxazolines **3**[9a,10] prompted us to explore the requirements necessary to achieve their selective formation. In addition, it was intriguing to investigate the chirality transfer in the reaction of chiral substrate **1** to 4-vinyloxazoline **3** as this could further extend the applications of imidate cyclization. The results of these investigations are summarized herein.

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## Results and Discussion

We had some preliminary information on the metal-catalysed cyclization of allylic imidates prior to this study as we had previously observed the selective formation of 4-vinyloxazoline **3** (R = H) as the major product in metal-catalysed reactions of trichloroacetimidate derived from (*Z*)-3-(benzyloxy)crotyl alcohol.[11] It has also been shown by Sabat and Johnson that bis-trichloroacetimidate derived from (*Z*)-butene-1,4-diol gives 4-vinyloxazoline **3** (R = H) as the main product when subjected to the $Pd^{II}$ catalyst, although this was assumed to be a $Pd^0$-catalysed reaction proceeding by the π-allyl mechanism.[9a] These observations implied that the *Z* configuration of the double bond is important to the course of the reaction. Indeed, imidate (*Z*)-**1a** gave exclusively 4-vinyloxazoline (*E*)-**3a** (Table 1, entry 1). It should be emphasized that the product (*E*)-**3a** was formed exclusively.

Table 1. $Pd^{II}$-catalysed formation of **2** and **3** depending on the configuration of the double bond of imidate **1** and the β-leaving group.[a]

| Entry | Imidate | R | $R^1$ | Yield of **3** [%] | Ratio **2**:**3**[b] |
|---|---|---|---|---|---|
| 1 | (*Z*)-**1a** | Me | TBS | 60 | <1:99 |
| 2 | (*E*)-**1a** | Me | TBS | not determined | 6:1[c] |
| 3 | (*Z*)-**1b** | *i*Pr | TBS | no reaction | – |
| 4 | (*Z*)-**1c** | *i*Pr | Ac | 88 | <1:99 |
| 5 | (*E*)-**1c** | *i*Pr | Ac | 62 | 1:2 |
| 6 | (*Z*)-**1g** | *n*-Hex | Boc | 100[d] | <1:99 |

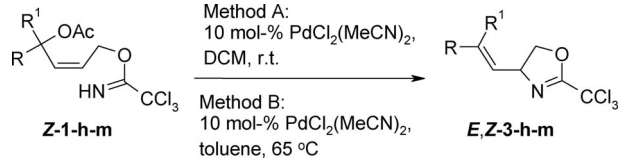
[a] Reagents and conditions: 10 mol-% $[PdCl_2(MeCN)_2]$ or $[PdCl_2(PhCN)_2]$, DCM, room temp., 12 h. [b] Determined by GC–MS. [c] Data from ref.[8]. [d] GC–MS and $^1H$ NMR conversion, no other products were detected.

Unfortunately, no reaction took place in the case of imidate (*Z*)-**1b** bearing a bulkier substituent (R = *i*Pr). This prompted us to search for a better β-leaving group. Several imidates (*Z*)-**1** (**c**: R = *i*Pr, $R^1$ = Ac; **d**: R = *i*Pr, $R^1$ = Me; **e**: R = *i*Pr, $R^1$ = Bn; **f**: R = *i*Pr, $R^1$ = H; **g**: R = *n*-Hex, $R^1$ = Boc) were prepared and subjected to the $[PdCl_2(MeCN)_2]$ or $[PdCl_2(PhCN)_2]$ catalyst. Only imidates (*Z*)-**1c**,**g** rearranged smoothly to give 4-vinyloxazolines (*E*)-**3c**,**g** in good yields. Notably, imidate (*Z*)-**1c** remained intact when exposed to $[Pd_2(dba)_3]$ and $[Pd(Ph_3P)_4]$ catalysts, which confirms $Pd^{II}$ catalysis in the cyclization of imidate **1**.

The importance of the configuration of the double bond in the reaction was again confirmed by using isomeric imidate (*E*)-**1c**. This substrate led to a mixture of the rearrangement product **2c** (*anti*/*syn* = 8:1) and the cyclization product **3c** (Table 1, entry 5).

The scope of 4-vinyloxazoline formation was investigated by expanding the range of substrates tested (Table 2). The reaction proceeded smoothly at room temperature with olefin substrates **1h**,**i** bearing a secondary δ-acetoxy group. However, a slightly higher temperature was beneficial to reach complete conversion in a shorter reaction time (Table 2, entries 1 and 2). Imidates **1j**,**k** bearing a δ-aryl group only reacted sufficiently fast at an increased temperature (entries 3–5). The cyclization of imidates (*Z*)-**1h**,**i**,**k** led to (*E*)-olefins (*E*)-**3h**,**i**,**k** exclusively, whereas in the case of imidate (*Z*)-**1j** the product (*E*)-**3j** was contaminated with the minor isomer (*Z*)-**3j**. Note that no other product formation was observed by $^1H$ NMR analysis of the crude products **3a**,**c**,**g**–**j** obtained from imidates (*Z*)-**1a**,**c**,**g**–**j**. The somewhat decreased yields are likely due to the low stability of products **3** on the silica gel used for separation from the catalyst.

Table 2. Formation of 4-vinyloxazolines **3** from structurally distinct *O*-allylic imidates **1**.




| Entry | Imidate | R | $R^1$ | Method, time [h] | Product(s), yield[a] [%] |
|---|---|---|---|---|---|
| 1 | (*Z*)-**1h** | *n*-Hex | H | A, 12 | (*E*)-**3h**, 83 |
| 2 | (*Z*)-**1i** | $BnOCH_2$ | H | B, 3 | (*E*)-**3i**, 73 |
| 3 | (*Z*)-**1j** | Ph | H | A, 4 | (*E*)-**3j**, 50[b] |
| 4 | (*Z*)-**1j** | Ph | H | B, 5 | (*E*)-,(*Z*)-**3j**, 73[c] |
| 5 | (*Z*)-**1k** | 9-Anthr.[d] | H | B, 4 | (*E*)-**3k**, 62 |
| 6 | (*Z*)-**1l** | Me | Me | A, 16 | **3l**, 30[e] (*E*)-**1l**, 15 |
| 7 | (*Z*)-**1l** | Me | Me | B, 2 | **3l**, 60 |
| 8 | (*Z*)-**1m** | Ph | Me | B, 3 | (*E*)-**3m**, 11 (*Z*)-**3m**, 16 |

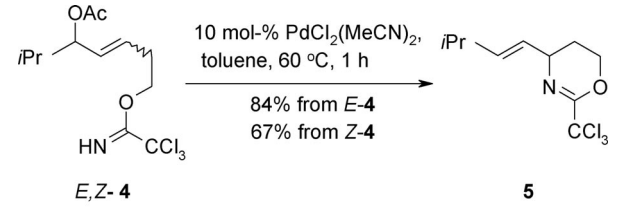
[a] Isolated yield. [b] 60% conversion by GC–MS. [c] *E*/*Z* = 94:6. [d] Anthracen-9-yl. [e] 100% conversion by GC–MS.

Imidates (*Z*)-**1l**,**m** bearing a tertiary δ-acetoxy group were more challenging substrates for the cyclization. Noteworthy, imidate (*Z*)-**1l** underwent complete isomerization to the *E* isomer (*E*)-**1l** within 2 h when exposed to the $Pd^{II}$ catalyst at room temperature as well as forming the cyclic imidate **3l** (Table 2, entry 6). Surprisingly, at a higher temperature, only 4-vinyloxazoline **3l** was observed and no Overman rearrangement product **2l** (entry 7). This indicates that imidates **1** bearing a tertiary δ-acetoxy group undergo 5-*exo* cyclization to form 4-vinyloxazolines **3** irrespective of the configuration of the double bond. Another similar substrate (*Z*)-**1m** gave a mixture of 4-vinyloxazoline isomers (*Z*)- and (*E*)-**3m** in low yields (entry 8) together with an oxazoline ring-opened byproduct.

The cyclization is not limited only to allylic imidates. Both (*E*)- and (*Z*)-ε-acetoxy-*O*-homoallylic trichloroacetimidates (*E*)- and (*Z*)-**4** underwent $Pd^{II}$-catalysed cyclization to give dihydrooxazine **5** (Scheme 2).

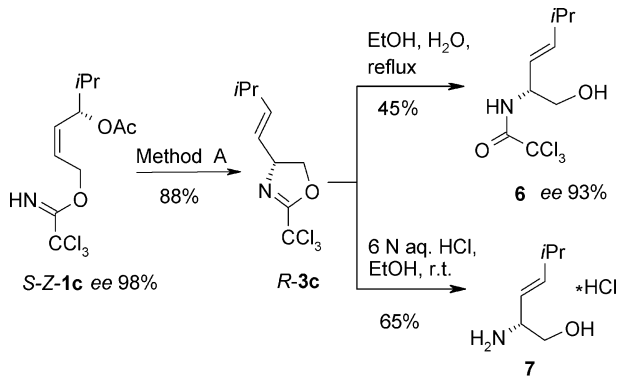
To explore the chirality transfer of imidate cyclization, homochiral substrate (*S*)-(*Z*)-**1c** was prepared by asymmetric addition of the *O*-protected propargyl alcohol to the aldehyde as the key step.[12] Imidate (*S*)-(*Z*)-**1c** was transformed into 4-vinyloxazoline (*R*)-(*E*)-**3c**, which was further hydrolysed to *N*-trichloroacetylamino alcohol derivative **6**, the *ee* of which could be determined by chiral HPLC (Scheme 3). The results indicated almost quantitative chi-



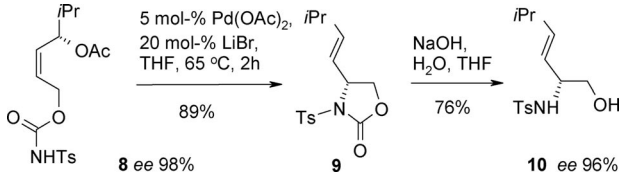

Scheme 2. Synthesis of dihydrooxazine **5**.

rality transfer from the substrate (*S*)-(*Z*)-**1c** to the product (*R*)-(*E*)-**3c**. The absolute configuration of the oxazoline (*R*)-(*E*)-**3c** was determined by transforming it into amino alcohol **7**, which in turn was derivatized with the chiral shift reagents (*R*)- and (*S*)-(5-fluoro-2,4-dinitrophenyl)(1-phenylethyl)amines (see the Supporting Information).[13]



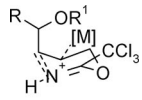

Scheme 3. Chirality transfer in imidate cyclization.

We established that the related cyclization of (*S*)-δ-acetoxy-*O*-allyl-*N*-tosylcarbamate **8**[7f] also proceeds with high chirality transfer, as determined by chiral HPLC analysis of *N*-tosylamino alcohol **10** derived from product **9** (Scheme 4). The cyclization product **9** had the same configuration as oxazoline (*R*)-**3c**, as was proven by transforming amino alcohol **7** into the same enantiomer of *N*-tosylamino alcohol **10**.




Scheme 4. Chirality transfer in tosylcarbamate cyclization.

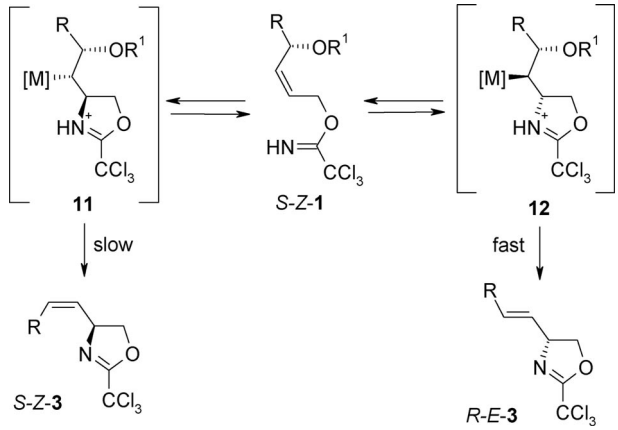
The studies of *O*-allyl imidate **1** cyclization have revealed that a *Z* configuration of the substrates bearing a secondary δ-oxy group is important for achieving selective formation of 4-vinyloxazoline **3**. This can be explained by a lower rate of the competitive Overman rearrangement due to the pseudo-axially situated substituent in the transition state **TS** of the 6-*endo trans*-aminopalladation of imidate (*Z*)-**1**, which is known to be the rate-limiting step for amide **2** formation (Figure 1).[14]




**TS** 6-*endo*

Figure 1. Proposed transition state for the 6-*endo* aminopalladation of imidate (*Z*)-**1**.

Both selective (*E*)-4-vinyloxazoline **3** formation and high chirality transfer from imidate (*S*)-(*Z*)-**1** to oxazoline (*R*)-(*E*)-**3** provided a basis for the discussion of the reaction mechanism. Assuming that the mechanism for oxazoline **3** formation is similar to the CIR mechanism of the Overman rearrangement it is unlikely that the stereoselectivity is directed by a chelation effect of the δ-oxy group. The results obtained show that the selectivity of (*E*)-olefin formation is not dependent on the oxygen substituent (Ac or TBS, Table 1). In addition, it is known for related *6-endo* aminopalladation that high selectivity (10:1) can be achieved only in the case of a special δ-directing group like *O*-MOM.[15] The observed stereochemical outcome can be explained by the mechanism of oxazoline (*R*)-(*E*)-**3** formation involving reversible stereospecific 5-*exo* aminopalladation followed by rate-limiting stereospecific deoxypalladation as the first irreversible step (Scheme 5). In this case one could expect deoxypalladation to occur faster from intermediate **12** giving the product (*R*)-(*E*)-**3**. The above considerations can also be used to explain the formation of *N*-tosyloxazolidinone **9** from carbamate **8**.




Scheme 5. Proposed mechanism for chirality transfer and (*E*)-olefin formation.

To explain the formation of 4-vinyloxazoline (*R*)-(*E*)-**3**, it was assumed that *anti* aminopalladation of the double bond occurs in analogy to the CIR mechanism of Overman rearrangement and is followed by *anti* deoxypalladation. Nevertheless, a *syn*-aminopalladation–*syn*-deoxypalladation mechanism cannot be completely ruled out without additional investigations as this would also lead to oxazoline (*R*)-(*E*)-**3** from imidate (*S*)-(*Z*)-**1**.

## Conclusions

Cyclization of trichloroacetimidates can be achieved by olefin aminopalladation/β-heteroatom elimination to provide 4-vinyloxazolines and a 4-vinyldihydrooxazines that are valuable precursors of amino alcohols and amino acids. For *O*-allyl imidates bearing a secondary δ-acetoxy group the *Z* configuration of the double bond is important for achieving selective 4-vinyloxazoline formation over competitive Overman rearrangement. The cyclization of trichloroacetimidates stereoselectively gives products with an *E* configuration of the double bond. By using a homochiral δ-acetoxy-*O*-allyl imidate it has been demonstrated that cyclization occurs with very high chirality transfer. Stereoselective (*E*)-4-vinyloxazoline formation and chirality transfer indicates that the mechanism involves stereospecific *anti* aminopalladation and *anti* deoxypalladation steps. We believe that trichloroacetimidate cyclization will find applications in the synthesis of complex natural products and pharmaceutically useful compounds.

## Experimental Section

**General:** The reagents and starting materials were obtained from commercial sources and used as received. The solvents were purified and dried by standard procedures prior to use; petroleum ether with a boiling range of 60–80 °C was used. All reactions were performed under argon. Flash chromatography was carried out using Merck Kieselgel (230–400 mesh). Thin-layer chromatography was performed on silica gel and was visualized by staining with $KMnO_4$. NMR spectra were recorded with a Varian Mercury spectrometer (600, 400 and 200 MHz) with chemical shifts values ($\delta$) in ppm relative to TMS with the residual chloroform signal as internal standard. Gas chromatographic analysis was performed by using the HP 6890 apparatus with a HP 5972 MSD detector. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. Melting points were determined with an OptiMelt Automated Melting Point System. HPLC analyses was performed with a Waters Alliance 2489 chromatographic system. Elemental analyses were performed on a Carlo–Erba Instrument EA1108 elemental analyser. HRMS spectra were obtained by using a Q-TOF micro high-resolution mass spectrometer in ESI mode ($ESI^+/ESI^-$).

The synthesis and characterization of imidates **1** and **4** and their precursors are given in the Supporting Information.

**General Procedure for the $Pd^{II}$-Catalysed Cyclization of Imidates**

**Method A:** A solution of trichloroacetimidate **1** (1 mmol) in DCM (6 mL) was flushed with argon and molecular sieves (4 Å) were added. The solution was stirred for 20 min and $[PdCl_2(CH_3CN)_2]$ (26 mg, 0.1 mmol) or $[PdCl_2(PhCN)_2]$ (38 mg, 0.1 mmol) was added. The mixture was stirred at room temp. until complete conversion of the starting material (ca. 24 h, TLC control, eluent: benzene) and then diluted with EtOAc (100 mL). The solution was washed with saturated aq. $NaHCO_3$ and dried with $Na_2SO_4$. The solvent was evaporated and the residue was purified by flash chromatography on silica gel, eluting with a mixture of EtOAc and light petroleum ether (1:8) to obtain the vinyloxazoline **3** and any other product if formed. Yields are given in Table 1 and Table 2.

**Method B:** A solution of trichloroacetimidate **1** or **4** (1 mmol) in toluene (6 mL) was flushed with argon and 4 Å molecular sieves were added. The solution was stirred for 20 min at room temp. and then $[PdCl_2(CH_3CN)_2]$ (26 mg, 0.1 mmol) was added. The mixture was heated at 65 °C until complete conversion of the starting material (TLC control, eluent: benzene) and then purified by silica gel column chromatography, eluting with a mixture of EtOAc and light petroleum ether (1:8) to obtain the vinyloxazoline **3** or vinyldihydrooxazine **5** and any other product if formed. Yields are given in Table 2.

**4-[(*E*)-Propenyl]-2-(trichloromethyl)-4,5-dihydrooxazole [(*E*)-3a]:** Compound (*E*)-**3a** is a known compound.[8]

**(1*s*,2*r*)-1-Isopropyl-2-(trichloroacetylamino)but-3-en-1-yl Acetate (2c):** Isolated as a byproduct in the cyclization of imidate (*E*)-**1c** as a colorless oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.60 (br. s, 1 H, =*NH*), 5.78 (ddd, $^3J$ = 16.1, $^3J$ = 10.3, $^3J$ = 5.9 Hz, 1 H, $CH_2$=*CH*-CH), 5.29 (m, 2 H, *CH*$_2$=CH), 4.67 [m, 2 H, *CH*(OAc), *CH*(CH=$CH_2$)NH], 2.11 [s, 3 H, C(=O)*CH*$_3$], 1.95 [octet, $^3J$ = 6.6 Hz, 1 H, *CH*($CH_3$)$_2$], 1.02 [t, $^3J$ = 6.6 Hz, 3 H, CH(*CH*$_3$)$_2$], 0.98 [t, $^3J$ = 6.6 Hz, 3 H, CH(*CH*$_3$)$_2$] ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 172.09, 161.17, 131.17, 118.69, 80.83, 55.07, 29.92, 29.69, 19.05, 18.30 ppm. GC–MS (EI): *m*/*z* (%) = 256 (1) [M – OAc]$^+$, 245 (2), 201 (16), 166 (14), 117 (10), 110 (9), 82 (12), 54 (10), 43 (100). For COSY and NOESY results, see the Supporting Information.

**(*E*)-4-(3-Methylbut-1-en-1-yl)-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole [(*E*)-3c]:** Colourless oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.73 [dd, $^3J$ = 15.3, $^3J$ = 6.4 Hz, 1 H, ($CH_3$)$_2$CH-*CH*=], 5.40 [ddd, $^3J$ = 15.3, $^3J$ = 7.4, $^4J$ = 1.2 Hz, 1 H, ($CH_3$)$_2$CH-CH=*CH*], 4.80 [m, 1 H -$CH_2$-*CH*(N=)-CH=], 4.74 (dd, $^3J$ = 9.8, $^3J$ = 8.2 Hz, 1 H, $CH_2$O), 4.29 (t, $^2J$, $^3J$ = 8.2 Hz, 1 H, $CH_2$-O), 2.31 [octet, $^3J$ = 6.7 Hz, 1 H, *CH*($CH_3$)$_2$], 1.01 [m, 6 H, CH(*CH*$_3$)$_2$] ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 162.78, 142.06, 124.51, 76.29, 68.83, 30.81, 21.98, 21.97 ppm. GC–MS (EI): *m*/*z* = 255 (1) [M]$^+$, 220 (35), 212 (17), 202 (14), 190 (21), 177 (12), 148 (20), 117 (21), 94 (31), 79 (66), 69 (54), 55 (44), 41 (100). HRMS (EI): calcd. for $C_9H_{13}Cl_3NO$ [M + H]$^+$ 256.0063; found 256.0022.

**(*R*)-(*E*)-4-(3-Methylbut-1-en-1-yl)-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole [(*R*)-(*E*)-3c]:** $[\alpha]_D^{20}$ = +101.3 (*c* = 9.5, DCM).

**(*E*)-4-(Oct-1-en-1-yl)-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole [(*E*)-3h]:** Colourless oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.75 (dt, $^3J$ = 15.3, $^3J$ = 6.9 Hz, 1 H, $CH_2$-*CH*=CH), 5.45 (dd, $^3J$ = 15.4, $^3J$ = 7.3 Hz, 1 H, $CH_2$-CH=*CH*), 4.80 [q, $^3J$ = 8.3 Hz, 1 H, =CH-*CH*(N=)], 4.74 (dd, $^3J$ = 9.8, $^2J$ = 8.2 Hz, 1 H, *CH*$_2$-O), 4.29 (t, $^2J$, $^3J$ = 8.2 Hz, 1 H, *CH*$_2$-O), 2.05 (q, $^3J$ = 6.6 Hz, 2 H, *CH*$_2$-CH=), 1.1–1.5 [m, 6 H, (*CH*$_2$)$_3$-], 0.88 (t, *J* = 6.6 Hz, 3 H, $CH_2$*CH*$_3$) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 162.76, 135.38, 127.20, 76.22, 68.72, 32.23, 31.34, 28.51, 22.45, 13.98 ppm. GC–MS (EI): *m*/*z* (%) = 155 (37) [M – Cl]$^+$, 240 (8), 226 (10), 214 (23), 201 (28), 178 (20), 166 (19), 148 (17), 119 (19), 93 (20), 82 (32), 67 (53), 55 (58), 41 (100). HRMS (EI): calcd. for $C_{11}H_{17}Cl_3NO$ [M + H]$^+$ 284.0376; found 284.0332.

**(*E*)-4-(3-Benzyloxyprop-1-en-1yl)-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole [(*E*)-3i]:** Colourless oil. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 7.2–7.5 (m, 5 H, Ar), 5.91 (dtd, $^3J$ = 15.5, $^3J$ = 5.1, $^4J$ = 0.8 Hz, 1 H, BnOCH$_2$-*CH*=), 5.78 (ddt, $^3J$ = 15.5, $^3J$ = 6.9, $^4J$ = 1.4 Hz, 1 H, $CH_2$-CH=*CH*), 4.89 [m, 1 H, =CH-*CH*(N=)], 4.76 (dd, $^3J$ = 9.8, $^2J$ = 8.2 Hz, 1 H, *CH*$_2$O), 4.54 (s, 2 H, Ph*CH*$_2$), 4.35 (t, $^3J$ = 8.4 Hz, 1 H, *CH*$_2$O-), 4.06 (d, $^3J$ = 4.4 Hz, 2 H, BnO*CH*$_2$-CH=) ppm. $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 163.13, 137.96, 130.52, 129.64, 128.40, 127.72, 127.69, 91.52, 75.93, 72.54, 69.70, 67.98 ppm. GC–MS (EI): *m*/*z* (%) = 298 (1) [M – Cl]$^+$, 242 (2), 227 (4), 191 (5), 146 (3), 117 (4), 91 (100), 78 (6), 65 (9). HRMS (EI): calcd. for $C_{14}H_{15}Cl_3NNaO_2$ [M + H]$^+$ 334.0168; found 334.0164.

**(*E*)-4-(2-Phenylvinyl)-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole [(*E*)-3j)]:** Compound (*E*)-**3j** is a known compound.[8]

**(*Z*)-4-(2-Phenylvinyl)-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole [(*Z*)-3j)]:** Obtained as a mixture with the *E* isomer. NMR spectra were recorded of the mixture of *E* and *Z* isomers. Colourless oil. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.2–7.5 (m, 5 H, Ar), 6.74 (d, $^3J$ = 11.3 Hz, 1 H, Ph-*CH*=), 5.68 (dd, $^3J$ = 11.0, $^2J$ = 9.5 Hz, 1 H, Ph-CH=*CH*), 5.05 [m, 1 H, =CH-*CH*(N=)$CH_2$O], 4.84 (dd, $^3J$ = 9.5, $^2J$ = 8.1 Hz, 1 H, *CH*$_2$O), 4.43 (t, $^3J$, $^2J$ = 8.4 Hz, 1 H, *CH*$_2$O) ppm. GC–MS (EI): *m*/*z* (%) = 289 (3) $[M]^+$, 255 (27), 224 (18), 182 (49), 154 (12), 142 (18), 128 (56), 115 (100), 104 (23), 91 (42), 77 (34), 63 (26), 51 (33), 39 (26).

**(*E*)-4-[2-(9-Anthryl)vinyl]-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole [(*E*)-3k)]:** Yellowish crystalline compound. M.p. 103–106 °C. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 8.39 (s, 1 H, Ar), 8.25 (m, 2 H, Ar), 7.99 (m, 2 H, Ar), 7.49 (m, 4 H, Ar), 7.43 (d, $^3J$ = 16.0 Hz, 1 H, Ar-*CH*=CH), 6.08 (dd, $^3J$ = 16.0, $^3J$ = 7.0 Hz, 1 H, Ar-CH=*CH*), 5.34 [m, 1 H, =CH-, *CH*(N=)], 4.97 (dd, $^3J$ = 9.4, $^2J$ = 8.2 Hz, 1 H, *CH*$_2$O-), 4.61 (t, $^3J$, $^2J$ = 8.1 Hz, 1 H, *CH*$_2$O) ppm. $^{13}$C NMR: $\delta$ = (100 MHz, $CDCl_3$): 163.57, 135.33, 131.27, 131.18, 129.31, 129.07, 128.64, 126.76, 125.60, 125.57, 125.12, 86.54, 76.21, 68.72 ppm. HRMS (EI): calcd. for $C_{20}H_{15}Cl_3NO$ $[M + H]^+$ 390.0219; found 390.0405.

**(*E*)-4-(2-Methylprop-1-en-1-yl)-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole (3l):** Colourless oil. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 5.16 [d, $^3J$ = 10.3 Hz, 1 H, $(CH_3)_2$C=*CH*], 5.05 [t, $^3J$ = 8.8 Hz, 1 H, =CH-*CH*(N=)], 4.75 (t, $^3J$, $^2J$ = 8.8 Hz, 1 H, *CH*$_2$O), 4.19 (t, $^3J$, $^2J$ = 8.8 Hz, 1 H, *CH*$_2$O), 1.75 [s, 3 H, $(CH_3)_2$C=], 1.73 [s, 3 H, $(CH_3)_2$-C=] ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 162.84, 137.56, 122.91, 76.67, 64.85, 51.87, 25.71, 18.45 ppm. GC–MS (EI): *m*/*z* (%) = 241 (1) $[M]^+$, 228 (4), 206 (18), 176 (22), 161 (24), 141 (14), 117 (12), 80 (100), 67 (32), 53 (31), 41 (60). Unstable in conditions used for HRMS determination.

**(*E*)-4-(2-Phenylprop-1-en-1-yl)-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole [(*E*)-3m)]:** Colourless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.2–7.5 (m, 5 H, Ar), 5.75 [d, $^3J$ = 9.0 Hz, 1 H, Ph(Me)C=*CH*], 5.28 [q, $^3J$ = 9.0 Hz, 1 H, =CH-*CH*(N=)], 4.87 (dd, $^3J$ = 10.0, $^2J$ = 8.2 Hz, 1 H, *CH*$_2$O), 4.33 (t, $^3J$, $^2J$ = 8.2 Hz, 1 H, *CH*$_2$O-), 2.15 (s, 3 H, *CH*$_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 163.26, 142.31, 139.54, 128.31, 127.65, 125.93, 125.63, 77.204, 65.28, 16.75 ppm. GC–MS (EI): *m*/*z* (%) = 303 (8) $[M]^+$, 288 (5), 268 (32), 238 (14), 196 (14), 156 (16), 142 (100), 128 (49), 115 (52), 103 (22), 91 (20), 77 (18), 51 (11). Unstable in conditions used for HRMS determination.

**(*Z*)-4-(2-Phenylprop-1-en-1-yl)-2-(trichloromethyl)-4,5-dihydro-1,3-oxazole [(*Z*)-3m)]:** Colourless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.2–7.5 (m, 5 H, Ph), 5.49 [dd, $^3J$ = 9.0, $^4J$ = 1.3 Hz, 1 H, Ph(Me)-C=*CH*], 4.86 [q, $^3J$ = 9.1 Hz, 1 H, =CH-*CH*(N=)], 4.62 (dd, $^3J$ = 9.7, $^2J$ = 8.6 Hz, 1 H, *CH*$_2$O), 4.25 (t, $^3J$, $^2J$ = 8.8 Hz, 1 H, *CH*$_2$O-), 2.10 (d, $^4J$ = 1.3 Hz, 3 H, *CH*$_3$) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 162.81, 141.97, 140.51, 128.38, 127.74, 127.45, 124.84, 75.57, 65.77, 25.46 ppm. GC–MS (EI): *m*/*z* (%) = 303 (5) $[M]^+$, 288 (5), 268 (34), 238 (14), 196 (16), 156 (17), 142 (100), 128 (56), 115 (54), 103 (22), 91 (20), 77 (21), 51 (13). HRMS (EI): calcd. for $C_{14}H_{15}Cl_3NNaO_2$ $[M + H_2O + Na]^+$ 343.9982; found 343.9986. For 2D NOESY, HSQC, HMBC results, see the Supporting Information

**(*E*)-4-(3-Methylbut-1-en-1-yl)-2-(trichloromethyl)-5,6-dihydro-4*H*-1,3-oxazine (5):** Colourless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.58 [ddd, $^3J$ = 15.5, $^3J$ = 6.3, $^4J$ = 1.2 Hz, 1 H, $(CH_3)_2$CH-*CH*=], 5.46 [ddd, $^3J$ = 15.5, $^3J$ = 5.5, $^4J$ = 0.8 Hz, 1 H, =*CH*-CH(N=)-$CH_2$], 4.38 (quintet, $J$ = 5.7 Hz, 2 H, *CH*$_2$O), 4.22 [q, $^3J$ = 5.4 Hz, 1 H, =CH-*CH*(N=)], 2.32 [octet, $^3J$ = 6.6 Hz, 1 H, *CH*$(CH_3)_2$], 2.06 (m, 1 H, *CH*$_2$-$CH_2$O), 1.73 (m, 1 H, *CH*$_2$$CH_2$O-), 1.00 [d, $^3J$ = 6.6 Hz, 6 H, CH(*CH*$_3$)$_2$] ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 153.42, 139.64, 126.93, 64.98, 52.91, 30.80, 26.65, 22.29, 22.27 ppm. GC–MS (EI): *m*/*z* (%) = 269 (1) $[M]^+$, 253 (1), 234 (100), 226 (33), 198 (19), 166 (26), 156 (15), 124 (26), 117 (34), 108 (40), 93 (74), 81 (44), 67 (20), 53 (33). HRMS (EI): calcd. for $C_{10}H_{15}Cl_3NO$ $[M + H]^+$ 270.0219; found 270.0155.

**(*R*)-*N*-(Trichloroacetyl)-[1-(hydroxymethyl)-4-methylpent-2-en-1-yl]-amine (6):** Water (1 mL) was added to the solution of oxazoline (*R*)-(*E*)-**3c** (103.0 mg; 0.4 mmol) in EtOH (3 mL). The mixture was heated at reflux for 18 h and then the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel, eluting with a mixture of EtOAc and light petroleum ether (1:3) to yield 50 mg (45%) of the amide **6** as a colourless crystalline compound with m.p. 41–42 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.01 (br. s, 1 H, *NH*), 5.74 [ddd, $^3J$ = 15.7, $^3J$ = 6.3, $^4J$ = 1.5 Hz, 1 H, $(CH_3)_2$CH-*CH*=], 5.41 [ddd, $^3J$ = 15.7, $^3J$ = 6.3, $^4J$ = 1.5 Hz, 1 H, =*CH*-CH(N=)], 4.48 [m, 1 H, =CH-*CH*(N=)], 3.76 (m, 2 H, *CH*$_2$OH), 2.33 [octet, $^3J$ = 6.7 Hz, 1 H, *CH*$(CH_3)_2$], 1.84 (t, $^3J$ = 5.5 Hz, 1 H, *OH*), 1.00 [d, $^3J$ = 7.0 Hz, 6 H, *CH*$(CH_3)_2$] ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 161.56, 141.97, 121.79, 92.66, 64.44, 54.52, 30.88, 22.14, 22.06 ppm. GC–MS (EI): *m*/*z* (%) = 255 (1) $[M – H_2O]^+$, 242 (26), 231 (1), 208 (11), 173 (4), 117 (6), 95 (15), 81 (100), 69 (14), 55 (13). HRMS (EI): calcd. for $C_9H_{14}Cl_3NNaO_2$ $[M + Na]^+$ 295.9988; found 295.9961. $[\alpha]_D^{20}$ = –8.1 (*c* = 1.3, DCM).

**(*R*)-[1-(Hydroxymethyl)-4-methylpent-2-en-1-yl]amine Hydrochloride (7):** Oxazoline (*R*)-**3c** (0.80 g; 3.1 mmol) was dissolved in a mixture of EtOH (15 mL) and 6 N aq. HCl (6 mL). The resulting mixture was stirred at room temperature for 12 h and the solvents evaporated. The residue was twice suspended in toluene (15 mL), the solvent evaporated and then treated with EtOAc (7 mL). The precipitate was collected on a filter and washed with additional EtOAc (3 mL). The product was dried in reduced pressure over $P_2O_5$ to give amino alcohol **7** (0.34 g, 65%) as a colourless very hygroscopic crystalline compound with m.p. 95–97 °C. $^1$H NMR (400 MHz, DMSO): $\delta$ = 8.12 (br. s, 3 H, $NH_3^+$), 5.77 [dd, $^3J$ = 15.8, $^3J$ = 6.3 Hz, 1 H, $(CH_3)_2$CH-*CH*=], 5.35 [ddd, $^3J$ = 15.8, $^3J$ = 7.0, $^4J$ = 1.2 Hz, 1 H, =*CH*-CH(N=)], 3.56 [m, 1 H, =CH-*CH*(N=)], 3.51 (dd, $^2J$ = 11.2, $^3J$ = 4.3 Hz, 1 H, *CH*$_2$OH), 3.43 (dd, $^2J$ = 11.2, $^3J$ = 7.2 Hz, 1 H, *CH*$_2$OH), 3.33 (br. s, 1 H, *OH*), 2.24 [octet of doublets, $^3J$ = 6.6, $^4J$ = 1.2 Hz, 1 H, *CH*$(CH_3)_2$], 0.92 [d, $^3J$ = 6.6 Hz, 6 H, CH(*CH*$_3$)$_2$] ppm. $^{13}$C NMR (100 MHz, DMSO): $\delta$ = 142.56, 120.90, 61.81, 54.17, 30.23, 21.73, 21.70 ppm. $C_7H_{16}ClNO{\cdot}H_2O$ (183.68): calcd. C 45.77, H 9.88, N 7.63; found C 45.43, H 9.46, N 7.63. $[\alpha]_D^{20}$ = –15.5 (*c* = 1.5, MeOH).

**(*S*)-(*Z*)-1-Isopropyl-4-[(*p*-tolylsulfonylcarbamoyl)oxy]but-2-en-1-yl Acetate (8):** *N*-Tosylcarbamate **8** was synthesized in analogy to the synthesis of the known racemic compound.[7f] Colourless amorphous solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.92 (d, $J$ = 8.1 Hz, 2 H, Ar), 7.58 (br. s, 1 H, *NH*Tos), 7.33 (d, $^3J$ = 8.1 Hz, 2 H, Ar), 5.63 (dt, $^3J$ = 11.3, $^3J$ = 6.4 Hz, 1 H, =*CH*-$CH_2$-O), 5.49 (ddt, $^3J$ = 11.3, $^3J$ = 9.3, $^4J$ = 1.5 Hz, 1 H, *CH*=CH-$CH_2$), 5.12 [dd, $^3J$ = 9.3, $^3J$ = 7.2 Hz, 1 H, *CH*(OAc)CH=], 4.79 (ddd, $^2J$ = 13.3, $^3J$ = 6.4, $^4J$ = 1.6 Hz, 1 H, *CH*$_2$O), 4.68 (ddd, $^2J$ = 13.3, $^3J$ = 6.5, $^4J$ = 1.6 Hz, 1 H, *CH*$_2$-O), 2.44 (s, 3 H, *CH*$_3$-$C_4H_6$), 2.04 [s, 3 H, C(=O)-*CH*$_3$], 1.80 [octet, $J$ = 7.0 Hz, 1 H, $(CH_3)_2$*CH*], 0.88 [d, $^3J$ = 7.0 Hz, 3 H, $(CH_3)_2$CH], 0.82 [d, $^3J$ = 7.0 Hz, 3 H, $(CH_3)_2$CH] ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 170.39, 150.08, 145.04, 135.40, 131.37, 129.56, 128.39, 126.70, 62.63, 31.93, 21.66, 21.06, 18.04,

17.81 ppm. GC–MS (EI): *m*/*z* (%) = 197 (30) $[TosNCO]^+$, 171 (1), 155 (53), 139 (2), 91 (100), 65 (24). HRMS (EI): calcd. for $C_{17}H_{23}NNaO_6S$ $[M + Na]^+$ 392.1144; found 392.1062. $[\alpha]_D^{20}$ = +10.1 (*c* = 2.0, DCM).

**(*R*)-(*E*)-4-(3-Methylbut-1-enyl)-3-(*p*-tolylsulfonyl)oxazolidin-2-one (9):** Compound **9** was synthesized in analogy to the known racemic compound.[7f] $[\alpha]_D^{20}$ = +31.7 (*c* = 0.7, DCM).

**(*R*)-*N*-(*p*-Tolylsulfonyl)-[1-(hydroxymethyl)-4-methylpent-2-en-1-yl]-amine (10)**

**From Oxazolidinone 9:** Compound **10** was synthesized from oxazolidinone **9** in analogy to the synthesis of the known racemic compound.[7f]

**From Amino Alcohol 7:** A suspension of amino alcohol **7** (35 mg, 0.21 mmol) in DCM (1 mL) was cooled to 0 °C in a cooling bath and TEA (44 mg, 60 μL, 0.43 mmol) was added followed by a solution of tosyl chloride (42 mg, 0.22 mmol) in DCM (1 mL). The cooling bath was removed and the mixture stirred at room temperature for 12 h. The solvent was removed in vacuo and the residue purified by flash chromatography on silica gel eluting the mixture of EtOAc and light petroleum ether (2:3) to give product **10** (57 mg, 95%) as a colourless crystalline compound with m.p. 54–55 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 7.74 (d, $^3J$ = 8.3 Hz, 2 H, Ar), 7.27 (d, $^3J$ = 8.3 Hz, 2 H, Ar), 5.37 [dd, $^3J$ = 15.5, 6.3 Hz, 1 H, $(CH_3)_2$-CH-*CH*=], 5.12 (s, 1 H, *NH*), 5.07 [ddd, $^3J$ = 15.5, $^3J$ = 7.0, $^4J$ = 1.2 Hz, 1 H, =*CH*-CH(N=)], 3.79 [m, 1 H, =CH-*CH*(N=)$CH_2$], 3.59 (dd, $^2J$ = 11.2, $^3J$ = 3.9 Hz, 1 H, $CH_2$OH), 3.50 (dd, $^2J$ = 11.2, $^3J$ = 6.5 Hz, 1 H, $CH_2$OH), 2.41 (s, 3 H, $CH_3$-$C_6H_4$), 2.26 (br. s, 1 H, *OH*), 2.08 [octet, $^3J$ = 6.7 Hz, 1 H, *CH*$(CH_3)_2$], 0.79 [d, $^3J$ = 6.6 Hz, 6 H, CH($CH_3$)$_2$] ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 143.37, 141.76, 137.65, 129.55, 127.26, 122.61, 65.33, 57.60, 30.58, 21.84, 21.79, 21.45 ppm. GC–MS (EI): *m*/*z* (%) = 283 (1) $[M]^+$, 267 (1), 252 (56), 236 (1), 171 (6), 155 (27), 139 (7), 112 (24), 97 (62), 91 (100), 82 (22), 65 (23). HRMS (EI): calcd. for $C_{14}H_{21}NNaO_3S$ $[M + Na]^+$ 306.1140; found 306.1125. $[\alpha]_D^{20}$ = +20.7 (*c* = 1.5, DCM).

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