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Electrochemical Oxidation of (*R*)-4-Hydroxy-2-pyrrolidone: A Key Building Block for Stereoselective *N*-Acyliminium Ion Coupling Reactions

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Abstract: The 5-methoxylation of (*R*)-4-hydroxy-2-pyrrolidone can be performed successfully by direct electrochemical oxidation at 40 mA/cm^2 in methanol at graphite electrodes using an undivided cell and sodium benzene sulfonate as supporting electrolyte. After direct protection of the intermediate as TBDMS ether, (4*R*)-4-*tert*-butyldimethylsilyloxy-5-methoxy-2-pyrrolidone **3** can be used in various diastereoselective amidoalkylation reactions. In most cases *cis*-stereoselectivity is observed. However, the favored *cis*-addition may be typical only for Si-organic compounds.

INTRODUCTION

The oxidation in α-position to the nitrogen atom of amides and carbamates to the corresponding α-oxy-compounds is a very important transformation in organic syntheses because of the use of such products as amidoalkylation reagents. The electrochemical methodology has been proven to be effective and simple for this oxidation process. Depending on the structure of the starting material direct anodic oxidation[1], indirect electrochemical oxidation processes[2] or the Hofer-Moest methoxylative decarboxylation of α-amino acids[3] can be applied. We were interested in the 5-methoxylation of commercially available (*R*)-4-hydroxy-2-pyrrolidone (**1**) by direct electrochemical oxidation. The product is a stable form of a chiral *N*-acyliminium ion which can be used to synthesize enantiopure 5-substituted pyrrolidone derivatives. These compounds are attractive synthetic targets which can be precursors for the synthesis of biological active polyhydroxylated monocyclic or bicyclic alkaloids[4].

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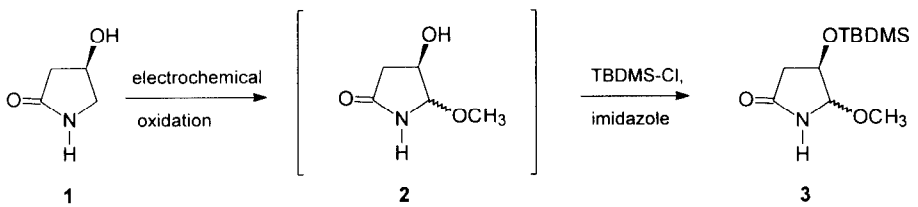
RESULTS AND DISCUSSION

Electrochemical oxidation of (R)-4-hydroxy-2-pyrrolidone **(1)**

For initial screening experiments **1** was oxidized using an undivided cell (10 ml) with a graphite anode and a platinum wire cathode (cond **I**, Table 1). The resulting α-methoxylated hydroxy-pyrrolidone **2** is a very polar, water soluble compound being difficult to isolate in pure form. Therefore, **2** was directly protected as TBDMS ether[5]. To optimize this two-step-procedure we studied the influence of the supporting electrolyte, the electrode material, the current density, and the concentration of starting material on the yield of the product. In all cases a mixture of *trans*- and *cis*-diastereomers was observed (*trans*:*cis*-ratio: 8:1).



1 **2** **3**

trans:*cis* 8:1

Scheme 1: Electrochemical oxidation of **1** and protection of the intermediate **2** as TBDMS ether **3**

Table 1: Conditions of the direct electrochemical oxidation of **1** to the intermediate **2** in methanol using an undivided cell (10 ml) and different supporting electrolytes until the consumption of 4 F/ mol of charge.

Cond.	Electrode Material	Current Density [mA/cm^2]	Conc. of Supporting Electrolyte [mol/l]	Conc. of Substrate [mol/l]
I	C-Anode (3cm^2)/ Pt-Wire-Cathode	40	0.1	0.1
II	C-Anode (3cm^2)/ C-Cathode (3cm^2)	40	0.1	0.1

The strong influence of the supporting electrolyte on product yields is outlined in Table 2. When salts like Bu_4NBF_4 or $NaBF_4$ were used only minor amounts of product could be isolated. Here, substantial quantities of starting material were recovered. On the other hand, the results for Et_4NOTs and especially for $PhSO_3Na$ were promising. In the latter case the oxidation proceeds at rt in 35% yield over two steps by simply changing the cathode material (cond. **II**, Table 1). The easiest way to explain these differences is the effect of the salts on the proton activity during the electrolysis. Best yields were obtained when the pH_{MeOH} is about 8-9 (sodium benzene sulfonate). At lower pH_{MeOH} (Bu_4NBF_4) methanol oxidation to give formaldehyde dimethyl

acetal maybe favored. This behaviour is in accordance with results previously reported for the electrochemical oxidation of a chiral 2-oxazolidinone[6].

Table 2: Effect of different supporting electrolytes on the yields of the α-methoxylated product (yields given after protection of the alcohol as TBDMS ether **3**).

No.	I	II	III	IV	V
Cond.	**I**	**I**	**I**	**I**	**II**
Supporting Electrolyte	Bu_4NBF_4	$NaBF_4$	Et_4NOTs	$PhSO_3Na$	$PhSO_3Na$
Material Yield [%]	5	13	16	23	35

Competition between amide and solvent oxidation also explains the effect of the current density on the product yield (Table 3). In principle, high current density should be desirable to shorten reaction time. In case of the oxidation of **1**, yields are constant in a range of 20-40 mA/cm^2. Higher currents decrease the product amounts drastically.

Table 3: Effect of the current density on the product yields applying condition **II** and $PhSO_3Na$ as supporting electrolyte (yields given after protection of the alcohol as TBDMS ether **3**).

No.	VI	VII	VIII	IX	X
Current Density [mA/cm^2]	20	30	40	50	60
Material Yield [%]	36	33	35	20	19

The solvent oxidation can be suppressed simply by using higher concentrations of substrate (Table 4, Figure 1). The yield of 57% of **3** in experiment No. XV is satisfying and can be obtained even on a large scale (5g, 50mmol). The reason for this concentration dependence is not fully understood[7]. So far an effective replacement of solvent molecules by starting material within the Helmholtz-layer or an electron hopping mechanism between substrate radical-cations and the starting material outside the Helmholtz-layer are discussed.

Table 4: Influence of the concentration of **1** on the anodic formation of **2** (yields given after protection of the alcohol as TBDMS ether **3**) applying cond. **II** and $PhSO_3Na$ as supporting electrolyte

No.	XI	XII	XIII	XIV	XV
Conc. of Substrate [mol/l]	0.1	0.3	0.5	0.7	0.83*
Material Yield [%]	35	34	45	55	57

*: saturated solution

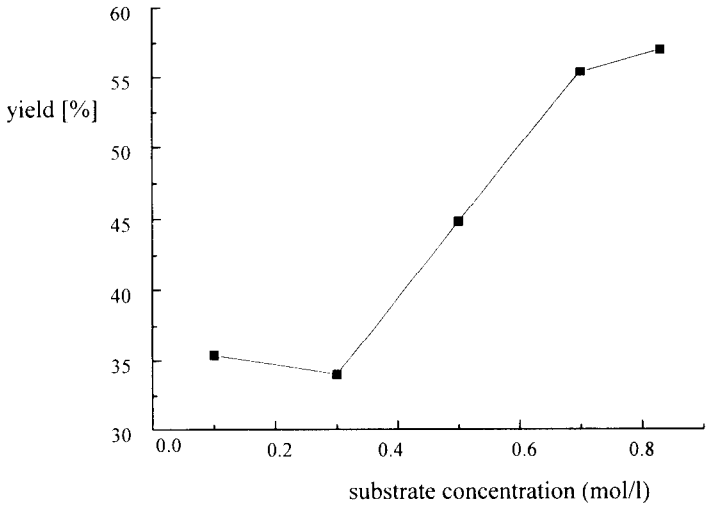
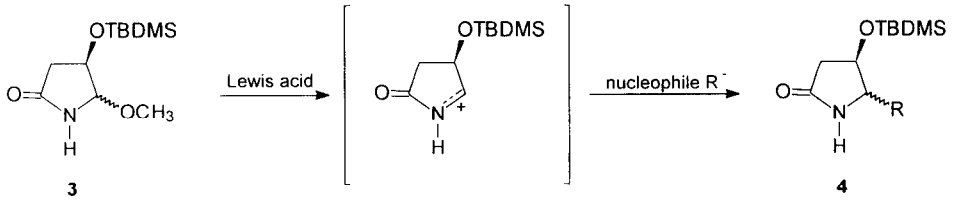


Figure 1: Correlation between the yield of **3** and the concentration of starting material **1**

N-Acyliminium ion coupling reactions

α-Methoxylated amides are stable precursors of *N*-acyliminium ions. Thus, **3** can undergo nucleophilic substitution of the methoxy group by carbon nucleophiles under catalysis of Lewis acids (Scheme 2)[8]. According to the literature, a proper choice of leaving group and Lewis acid is crucial. In case of **3** $TiCl_4$ seems to be necessary as Lewis acid (Table 5 and 6, Method A and C). Other Lewis acids like BF_3-etherate or rare earth triflates ($Yb(OTf)_3$) are not effective in generating the *N*-acyliminium intermediate. Only a modified procedure using BF_3-etherate and acetic anhydride[9] can also be applied in this case (Table 5 and 6, Method B).

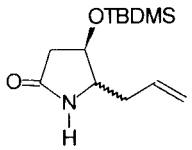
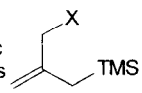
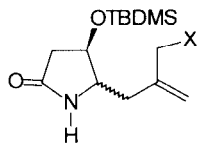
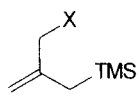
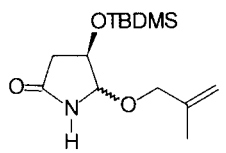
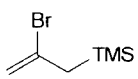
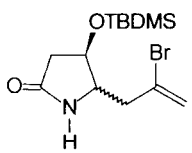


Scheme 2: Nucleophilic substitution of the α-methoxylated pyrrolidone **3** under the catalysis of Lewis acids

In order to study the scope and limitations of the substitution reactions under the conditions mentioned above several substituted allylsilanes were tested for their reactivity (Table 5). Except in one case, C-substitution gave rise to amides **4a-c** and **4e** in good *cis*-selectivity and moderate to good material yields. In case of the 2-

methanesulfoxymethyl-substituted allylsilane (entry 4) an additional undesired substitution of the MsO group took place. Interestingly, the unprotected 2-hydroxymethyl-allyltrimethylsilane only led to transacetalization under loss of the TMS group (entry 5). Here *trans*-selectivity is obvious.

Table 5: Nucleophilic substitution of the methoxy group in **3** by different substituted allyltrimethylsilanes

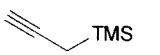
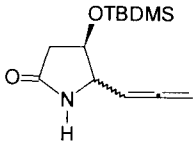
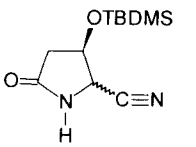
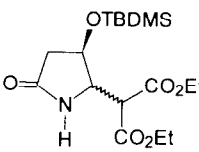
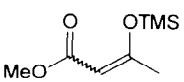
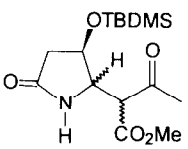
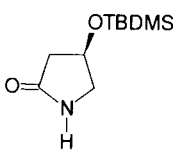
Entry	Method	(substituted) Allyltrimethylsilane	Product	Yield
1	A		 **4a**	**89% (ds: 83% *cis*)**
2	A X = Cl		 X = Cl **4b**	**85% (ds: 86% *cis*)**
3	A X = OAc		X = OAc **4c**	**34% (ds: 87% *cis*)**
4	A X = OMs		X = Cl **4b**	**37% (ds: 80% *cis*)**
5	A X = OH		 **4d**	**44% (ds: 78% *trans*)**
6	A		 **4e**	**72% (ds: 73% *cis*)**

method A: $TiCl_4$ (1.5 equiv), nucleophile (2 equiv), CH_2Cl_2, -78°C (4h) - rt (1-2d)

The *cis*-selectivity in the coupling reactions was somewhat unexpected and therefore the effect of other types of nucleophiles was studied. Propargyltrimethylsilane (Table 6, entry 7), trimethylsilylcyanide (entry 8) and a silyl enol ether (entry 10) also exhibited good *cis*-selectivity. In this series only the titanium enolate prepared in situ from diethyl malonate (entry 9) gave predominantly the *trans* product. This observation is remarkable. Obviously, the same kind of nucleophile (entry 9 and 10) adds in stereochemically different ways depending on the metal centre used in the enolate. To our knowledge, this influence is without precedent and the reason for that is presently unknown. Wistrand[10] and Seebach[11] investigated similar transformations with protected 3-

and 4-hydroxy-2-methoxy-1-methoxycarbonylpyrrolidine and also found *cis*-selectivity for the O-TBDMS protected derivatives. Furthermore *cis*-stereoselectivity has been observed for Lewis acid induced substitution reactions with allylstannanes in the case of C-3 and C-4 O-TBDMS protected 5-acetoxy-2-pyrrolidones[12]. In all these cases no significant change in the direction of addition depending on the nature of the nucleophile has been found.

Table 6: Si- and Ti-organic compounds as nucleophiles in amidoalkylation reactions with **3**

Entry	Method	Nucleophile	Product		Yield
7	B			**4f**	**23% (ds: 87% *cis*)**
8	A	TMS—C≡N		**4g**	**55% (ds: 77% *cis*)**
9	C	$CH_2(CO_2Et)_2$		**4h**	**66% (ds: 80% *trans*)**
10	A			**4i**	**52% (ds: 81% *cis*)** **1.3:1 mixture of C-1′ isomers**
11	A	Et_3SiH		**4j**	**37%**

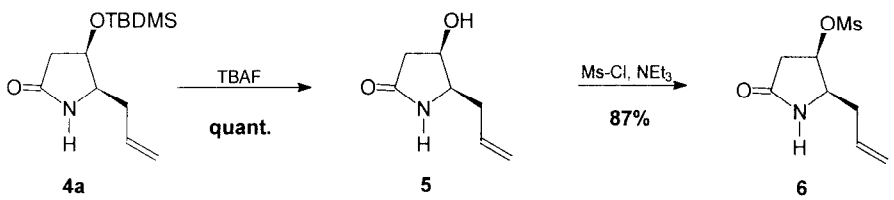
method A: $TiCl_4$ (1.5 equiv), nucleophile (2 equiv), CH_2Cl_2, -78°C (4h) - rt (1-2d)

method B: BF_3*OEt_2 (1.5 equiv), Ac_2O (1 equiv), nucleophile (2 equiv), CH_2Cl_2, -20°C (4h) - rt (3d)

method C: $TiCl_4$ (3 equiv), NEt_3 (1.7 equiv), nucleophile (2 equiv), CH_2Cl_2, -78°C (4h) - rt (1d)

*Configuration determination of cis-***4a**

A verification of the configuration of *cis*-**4a** was also performed. Thus, **4a** was quantitatively deprotected to the corresponding alcohol **5**. Transformation into its *R*-(+)-MTPA ester[13] confirmed the enantiomeric purity of the amidoalkylation product. The optical purity of these products could also be proved by comparison of the optical rotations of **4j** prepared by simply protecting starting material **1** ($[\alpha]_{25}^{D}$ = +19.8°, c = 1.0, EtOH) and by reduction of compound **3** with Et_3SiH under the conditions of *N*-acyl imiminium ion coupling reactions (Table 6, entry 11) ($[\alpha]_{25}^{D}$ = +20.4°, c = 1.01, EtOH). Reaction of **5** with methanesulfoxy chloride and triethylamine led in 87% yield to compound **6**.



Scheme 3: Synthesis of a 4-methanesulfoxy derivative of *cis*-**4a**

Furthermore, an X-ray crystal structure analysis of **6** (Figure 2)[14] confirmed the *cis* relationship between the allyl and the O-TBDMS functionalities. The stereochemistry of compounds **4b-4i** could be easily determined by comparison of typical chemical shifts and coupling constants to those in *cis*- and *trans*-**4a** (Table 7).

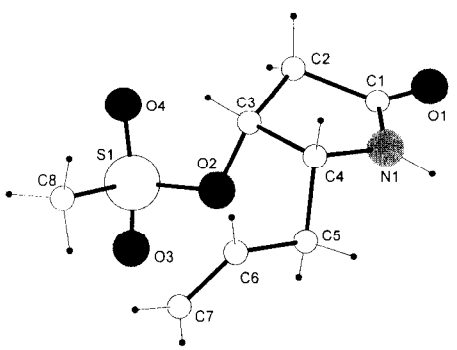
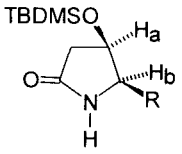
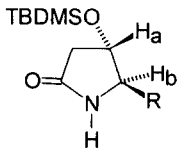


Figure 2: X-ray crystal structure analysis of **6**

Table 7: Determination of the relative configuration in *cis/trans*-**4a-i** by comparison of typical chemical shifts and coupling constants



***cis*-4**



***trans*-4**

compound	δH_a [ppm]	$^3J_{ab}$ [Hz]	compound	δH_a [ppm]	$^3J_{ab}$ [Hz]
4a	4.40	5.7	**4a**	4.06	3.7
4b	4.43	5.5	**4b**	4.04	4.2
4c	4.41	5.4	**4c**	4.04	4.2
4d[a]	-	-	**4d**	4.20	1.0
4e	4.46	5.9	**4e**	4.05	4.2
4f	4.43	6.2	**4f**[a]	-	-
4g	4.64	6.4	**4g**[a]	-	-
4h	4.55	5.2	**4h**	4.34	2.9
4i	4.60	5.4/ 5.9	**4i**	-	-

a: only main isomer characterized

EXPERIMENTAL

General. All compounds are identified by microanalysis or high resolution mass spectrometry, ^{1}H NMR, ^{13}C NMR and mass spectrometry. Nuclear magnetic resonance (^{1}H NMR) spectra were determined in the reported solvent using a Bruker AC 400 (400 MHz) spectrometer. The same instrument was also used for the measurements of ^{13}C spectra (100.6 MHz). Chemical shifts are given in ppm downfield from tetramethylsilane. Mass or FABMS spectra were obtained using A.E.I. MS-50 and MS-30 or Kratos MS-50 spectrometers. R_f values were obtained by using thin-layer chromatography (TLC) on silica gel-coated plastic sheets (Merck silica gel F_{254}). All solvents were distilled before using. All *N*-acyliminium ion coupling reactions were carried out under an inert atmosphere of dry argon. The *cis:trans* ratios were determined by careful analysis of the ^{1}H spectra of the crude products.

General procedure for the electrolyses

Starting material, supporting electrolyte and solvent are placed in an undivided water-cooled beaker type glass cell of 10 ml volume equipped with graphite anode and cathode of equal size (Pt wire cathode in some cases). The electrolyses were performed under stirring at rt and constant current. After the electrolysis is stopped, the solvent is removed in vavuo and the resulting oil is protected as TBDMS ether without further purification. Preparation of the electrodes: graphite electrodes were prepared as follows: 1. aceton (ultrasound 5 min); 2. methanol (ultrasound 5 min); 3. methanol p.a. (ultrasound 5 min). Pt wire electrodes were cleaned by glowing. All electrolyses were performed in methanol p.a.

***trans*- and *cis*-(4*R*)-4-*tert*-Butyldimethylsilyloxy-5-methoxy-2-pyrrolidone (3).** A solution of (*R*)-4-hydroxy-2-pyrrolidone **(1)** (838 mg, 8.3 mmol) and of $PhSO_3Na$ (180 mg, 1 mmol) in 10 ml of methanol p.a. was electrolyzed at a current density of 40 mA/cm^2 at rt 15°C until the consumption of 4 F/mol. After work-up the crude product was dissolved in 5 ml of DMF. Imidazole (1.08 g, 15.8 mmol) and *tert*-butyldimethylsilyl chloride (1.83 g, 11.6 mmol) were added, and the mixture was stirred at rt overnight. After dilution with Et_2O (50 ml), the solution was washed with water, dried over Na_2SO_4, and filtered. After concentration in vacuo, flash chromatography (EtOAc/cyclohexane 1:1) afforded 1.15 g of **3** (57% (*trans*:*cis* 8:1)). Mp: 99-101°C (white crystals, *trans*), 130-135°C (yellow crystals, *cis*). R_f: 0.46 (*trans*), 0.42 (*cis*) (EtOAc/cyclohexane 1:1). $[\alpha]_{25}^{D}$ = -31.2° (c = 1.03, EtOH) (*trans*), -9.9° (c = 1.19, EtOH) (*cis*). ^{1}H NMR ($CDCl_3$): *trans*: δ = -0.01, 0.00 (2s, 6H, $2CH_3$), 0.78 (s, 9H, $C(CH_3)_3$), 2.02 (d, J = 17.2Hz, 1H, CH_2), 2.62 (dd, J = 17.4, 5.9Hz, 1H, CH_2), 3.24 (s, 3H, OCH_3), 4.16 (d, J = 5.4Hz, 1H, CHO), 4.49 (s, 1H, CHN), 7.56 (brs, 1H, NH); *cis*: δ = 0.00, 0.01 (2s, 6H, $2CH_3$), 0.81 (s, 9H, $C(CH_3)_3$), 2.33 (dd, J = 16.2, 7.9Hz, 1H, CH_2), 2.40 (dd, J = 16.2, 9.1Hz, 1H, CH_2), 3.30 (s, 3H, OCH_3), 4.33 (ddd, J = 9.1, 7.9, 5.0Hz, 1H, CHO), 4.55 (d, J = 5.0Hz, 1H, CHN), 7.70 (brs, 1H, NH). ^{13}C NMR ($CDCl_3$): *trans*: δ = -4.9, -4.8, 18.0, 25.7, 38.9, 55.0, 72.6, 94.0, 177.7; *cis*: δ = -3.0, 18.1, 25.6, 37.1, 55.3, 69.7, 87.1, 176.6. MS (FAB, mNBA) m/z = 246.2 (M^++H). Anal. found C, 53.44; H, 9.32; N, 5.91. Calculated for $C_{11}H_{23}NO_3Si$: C, 53.84; H, 9.45; N, 5.71.

General procedure for the N-Acyliminium ion coupling of **3**:

Method A: To a solution of **3** (245 mg, 1 mmol) in 10 ml CH_2Cl_2 1.5 ml of a 1 M solution of $TiCl_4$ in CH_2Cl_2 (1.5 mmol) were added at -78°C. After 15 min 2 equivalents of the nucleophile were added. The solution was stirred at -78°C for 4 h, and was then allowed to warm to rt. After stirring for an additional 1 or 2 d, the Lewis acid was hydrolyzed by adding a saturated aqueous solution of $NaHCO_3$, and the mixture was extracted three times with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography (EtOAc/cyclohexane 1:1) afforded the separated diastereomers of **4**.

Method B: To a solution of **3** (245 mg, 1 mmol) in 10 ml CH_2Cl_2 acetic anhydride (0.1 ml, 1 mmol) and BF_3-etherate (0.27 ml, 2 mmol) were added at -20°C. After 10 min 2 equivalents of the nucleophile were added. The solution was stirred at -20°C for 4 h, and was then allowed to warm to rt. After stirring for 3 d, the Lewis acid was hydrolyzed by the addition of a saturated aqueous solution of $NaHCO_3$, and the mixture was extracted three times with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography (EtOAc/cyclohexane 1:1) afforded the separated diastereomers of **4**.

Method C: To a solution of **3** (245 mg, 1 mmol) in 10 ml CH_2Cl_2 3 ml of a 1 M solution of $TiCl_4$ in CH_2Cl_2 (3 mmol) were added at -78°C. After 15 min 2 equivalents of the nucleophile and an additional 5 min later triethylamine (0.24 ml, 1.7 mmol) were added. The solution was stirred at -78°C for 4 h, and was then allowed to warm to rt. After stirring for 1 d, the Lewis acid was hydrolyzed by adding a saturated aqueous solution of $NaHCO_3$, and the mixture was extracted three times with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography (EtOAc/cyclohexane 1:1) afforded the separated diastereomers of **4**.

***cis*- and *trans*-(4*R*)-5-Allyl-4-*tert*-butyldimethylsilyloxy-2-pyrrolidone (4a).** **4a** was synthesized according to method A using 0.33 ml of allyltrimethylsilane as nucleophile. Yield: 227 mg of **4a** (89%, ds (*cis*): 83%). Mp: 78-81°C (white crystals, *cis*), 40-45°C (yellow crystals, *trans*). R_f: 0.26 (*cis*), 0.30 (*trans*) (EtOAc/cyclohexane 1:1). $[\alpha]_{25}^{D}$ = +11.6° (c = 1.03, EtOH) (*cis*), -12.8° (c = 1.09, EtOH) (*trans*). ^{1}H NMR ($CDCl_3$): *cis*: δ = 0.00 (s, 6H, $2CH_3$), 0.82 (s, 9H, $C(CH_3)_3$), 2.17 (ddd, J = 14.3, 9.4, 8.4Hz, 1H, CH_2), 2.23 (d, J = 16.7, 4.2Hz, 1H, CH_2), 2.30 (ddd, J = 14.3, 5.8, 4.2Hz, 1H, CH_2), 2.51 (dd, J = 16.7, 6.4Hz, 1H, CH_2), 3.59 (ddd, J = 9.4, 5.7, 4.2Hz, 1H, CHN), 4.38-4.42 (m, 1H, CHO), 5.05-5.10 (m, 2H, $=CH_2$), 5.72 (dddd, J = 17.1, 10.1, 8.4, 5.8Hz, 1H, =CH), 6.42 (brs, 1H, NH); *trans*:δ = -0.01, 0.00 (2s, 6H, $2CH_3$), 0.82 (s, 9H, $C(CH_3)_3$), 2.04 (dt, J = 14.0, 8.1Hz, 1H, CH_2), 2.21 (dd, J = 17.0, 5.2Hz, 1H, CH_2), 2.29-2.35 (m, 2H, CH_2), 2.54 (dd, J = 17.0, 5.9Hz, 1H, CH_2), 3.40-3.45 (m, 1H, CHN), 4.06 (ddd, J = 6.7, 5.2, 3.7Hz, 1H, CHO), 5.05-5.09 (m, 2H, $=CH_2$), 5.70 (dddd, J = 16.7, 10.6, 8.1, 6.2Hz, 1H, =CH), 6.30 (brs, 1H, NH). ^{13}C NMR ($CDCl_3$): *cis*: δ = -5.0, -4.6, 18.1, 25.7, 34.2, 40.7, 59.0, 69.1, 118.4, 134.4, 175.6; *trans*: δ = -4.8, -4.6, 17.9, 25.7, 38.3, 40.4, 62.5, 72.5, 118.7, 133.5, 175.2. MS (FAB, mNBA) m/z = 256.2 (M^++H). Anal. found C, 61.11; H, 9.91; N, 5.36. Calculated for $C_{13}H_{25}NO_2Si$: C, 61.13; H, 9.86; N, 5.48.

***cis*- and *trans*-(4*R*)-4-*tert*-Butyldimethylsilyloxy-5-(2-chloromethyl-2-propenyl)-2-pyrrolidone (4b).** **4b** was synthesized according to method A using 0.36 ml of 2-chloromethyl allyltrimethylsilane as nucleophile. The minor *trans* diastereomer could only be characterized by NMR. Yield: 257 mg of **4a** (85%, ds (*cis*): 86%). Mp: 101-105°C (white crystals, *cis*), colorless oil (*trans*). R_f: 0.26 (*cis*), 0.29 (*trans*) (EtOAc/cyclohexane 1:1). $[\alpha]_{25}^{D}$ = +6.0° (c = 1.0, EtOH) (*cis*). ^{1}H NMR ($CDCl_3$): *cis*: δ = 0.00 (s, 6H, $2CH_3$), 0.81 (s, 9H, $C(CH_3)_3$), 2.24 (dd, J = 16.7, 4.1Hz, 1H, CH_2), 2.25 (dd, J = 15.0, 10.6Hz, 1H, CH_2), 2.44 (dd, J = 15.0, 2.8Hz, 1H, CH_2), 2.51 (dd, J = 16.7, 6.1Hz, 1H, CH_2), 3.80 (ddd, J = 10.6, 5.5, 3.4Hz, 1H, CHN), 3.94, 4.00 (2d, J = 12.0Hz, CH_2Cl), 4.43 (ddd, J = 6.0, 5.8, 4.1Hz, 1H, CHO), 4.98, 5.19 (2s, 2H, $=CH_2$), 5.67 (brs, 1H, NH); *trans*:δ = -0.01, 0.00 (2s, 6H, $2CH_3$), 0.81 (s, 9H, $C(CH_3)_3$), 2.11 (dd, J = 14.6, 9.6Hz, 1H, CH_2), 2.24 (dd, J = 16.9, 5.4Hz, 1H, CH_2), 2.50 (dd, J = 14.8, 3.7Hz, 1H, CH_2), 2.57 (dd, J = 16.7, 7.1Hz, 1H, CH_2), 3.53-3.60 (m, 1H, CHN), 3.98 (s, 2H, CH_2Cl), 4.04 (ddd, J = 7.1, 5.4, 4.2Hz, 1H, CHO), 4.99, 5.19 (2s, 2H, $=CH_2$), 5.87 (brs, 1H, NH). ^{13}C NMR ($CDCl_3$): *cis*: δ = -5.0, -4.6, 18.1, 25.7, 34.0, 40.5, 48.0, 56.8, 69.4, 117.7, 141.9, 175.0; *trans*: δ = -4.8, -4.5, 17.9, 25.7, 38.1, 40.3, 47.7, 60.8, 73.2, 117.8, 141.2, 174.7. MS (EI) m/z = 304 (M^++H), 288 (M^+-CH_3). HRMS calculated for $C_{14}H_{27}ClNO_2Si$ (M^++H) 304.1499, found 304.1445. Anal. found C, 54.90; H, 8.48; N, 4.40. Calculated for $C_{14}H_{26}ClNO_2Si$: C, 55.33; H, 8.62; N, 4.61.

***cis*- and *trans*-(4*R*)-5-(2-Acetoxymethyl-2-propenyl)-4-*tert*-butyldimethylsilyloxy-2-pyrrolidone (4c).** **4c** was synthesized according to method A using 0.42 ml of 2-acetoxymethyl allyltrimethylsilane as nucleophile. Yield: 111 mg of **4c** (34%, ds (*cis*): 87%). Colorless oil (*cis* and *trans*). R_f: 0.16 (*cis*), 0.20 (*trans*) (EtOAc/cyclohexane 1:1). $[\alpha]_{25}^{D}$ = +7.6° (c = 1.03, EtOH) (*cis*), -3.4° (c = 0.8, EtOH) (*trans*). ^{1}H NMR ($CDCl_3$): *cis*: δ = -0.01, 0.00 (2s, 6H, $2CH_3$), 0.81 (s, 9H, $C(CH_3)_3$), 2.02 (s, 3H, CH_3), 2.17 (dd, J = 14.8, 10.6Hz, 1H, CH_2), 2.22 (dd, J = 16.7, 4.4Hz, 1H, CH_2), 2.26 (dd, J = 14.8, 4.0Hz, 1H, CH_2), 2.48 (dd, J = 16.7, 6.4Hz, 1H, CH_2), 3.73 (ddd, J = 10.6, 5.4, 4.0Hz, 1H, CHN), 4.39-4.44 (m, 1H, CHO), 4.43, 4.49 (2d, J = 13.3Hz, CH_2OAc), 4.96, 5.10 (2s, 2H, $=CH_2$), 6.02 (brs, 1H, NH); *trans*: δ = 0.00 (s, 6H, $2CH_3$), 0.81 (s, 9H, $C(CH_3)_3$), 2.00 (dd, J = 14.3, 9.6Hz, 1H, CH_2), 2.03 (s, 3H, CH_3), 2.27 (dd, J = 17.0, 5.4Hz, 1H, CH_2), 2.26 (dd, J = 14.3, 4.2Hz, 1H, CH_2), 2.59 (dd, J = 17.0, 6.9Hz, 1H, CH_2), 3.55 (dt, J = 9.8, 4.2Hz, 1H, CHN),

4.04 (ddd, J = 6.7, 5.4, 4.2Hz, 1H, CHO), 4.98, 5.13 (2s, 2H, $=CH_2$), 5.95 (brs, 1H, NH). ^{13}C NMR ($CDCl_3$): *cis*: δ = -5.1, -4.7, 18.0, 20.9, 25.7, 33.8, 40.4, 57.0, 66.6, 69.3, 115.5, 140.7, 170.7, 175.1; *trans*: δ = -4.9, -4.6, 17.9, 20.9, 25.7, 38.3, 40.3, 61.0, 66.4, 73.3, 116.1, 140.0, 170.6, 174.6. MS (FAB, mNBA) m/z = 328.2 (M^++H). Anal. found C, 58.61; H, 8.88; N, 4.13. Calculated for $C_{16}H_{29}NO_4Si$: C, 58.68; H, 8.93; N, 4.28.

***cis*- and *trans*-(4*R*)-4-*tert*-Butyldimethylsilyloxy-5-(2-methyl-allyloxy)-2-pyrrolidone (4d).** **4d** was synthesized according to method A using 288 mg of 2-hydroxymethyl allyltrimethylsilane as nucleophile. 115 mg of starting material were recovered. The minor *cis* diastereomer could not be isolated and characterized. Yield: 92 mg of **4d** (44%, ds (*trans*): 78%). Mp: 82-85°C (white crystals, *trans*). R_f: 0.21 (*trans*), 0.24 (*cis*) (EtOAc/cyclohexane 1:1). $[\alpha]_{25}^{D}$ = -31.8° (c = 0.58, EtOH) (*trans*). ^1H NMR ($CDCl_3$, mixture of rotamers): *trans*: δ = -0.01, 0.00, 0.01 (3s, 6H, $2CH_3$), 0.78, 0.79 (2s, 9H, $C(CH_3)_3$), 1.45, 1.46 (2brs, 3H, CH_3), 2.03, 2.05 (2dd, J = 17.2, 1.7Hz, 1H, CH_2), 2.64 (dd, J = 17.2, 6.2Hz, 1H, CH_2), 3.39 (d, J = 9.8Hz, 0.5H, CH_2), 3.49 (d, J = 9.8Hz, 0.5H, CH_2), 3.79 (d, J = 12.3Hz, 0.5H, CH_2), 3.88 (d, J = 12.3Hz, 0.5H, CH_2), 4.20, 4.23 (2ddd, J = 6.2, 1.7, 1.0Hz, 1H, CHO), 4.60, 4.68 (2d, J = 1.0Hz, 1H, CHN), 4.84, 4.91 (2s, 2H, $=CH_2$), 6.88, 6.96 (2brs, 1H, NH). ^{13}C NMR ($CDCl_3$, mixture of rotamers): *trans*: δ = -4.9 (1C), -4.8 (1C), 18.0 (0.5C), 19.5 (0.5C), 25.7 (3C), 29.2 (0.5C), 29.3 (0.5C), 38.8 (0.5C), 38.9 (0.5C), 71.9 (0.5C), 72.4 (0.5C), 72.9 (0.5C), 73.1 (0.5C), 92.1 (0.5C), 93.4 (0.5C), 113.4 (1C), 141.4 (1C), 177.0 (0.5C), 177.2 (0.5C). MS (EI) m/z = 285 (M^+), 228 (M^+-C_4H_9). HRMS calculated for $C_{14}H_{27}NO_3Si$ 285.1760, found 285.1765.

***cis*- and *trans*-(4*R*)-5-(2-Bromoallyl)-4-*tert*-butyldimethylsilyloxy-2-pyrrolidone (4e).** **4e** was synthesized according to method A using 0.33 ml of 2-bromoallyl-trimethylsilane as nucleophile. The diastereomers could not be separated by chromatography. Yield: 286 mg of **4e** (72%, ds (*cis*): 73%). Colorless oil (*cis* and *trans*). R_f: 0.30 (*cis* and *trans*) (EtOAc/cyclohexane 1:1). ^1H NMR ($CDCl_3$, mixture of rotamers): *cis*: δ = -0.02 (s, 6H, $2CH_3$), 0.81 (s, 9H, $C(CH_3)_3$), 2.20 (dd, J = 16.7, 4.7Hz, 1H, CH_2), 2.45-2.56 (m, 2H, CH_2), 2.50 (dd, J = 16.7, 6.6Hz, 1H, CH_2), 3.89 (ddd, J = 8.6, 5.9, 4.7Hz, 1H, CHN), 4.43-4.50 (m, 1H, CHO), 5.47, 5.48 (2d, J = 1.8Hz, 1H, $=CH_2$), 5.60, 5.64 (2brs, 1H, $=CH_2$), 5.70 (brs, 1H, NH); *trans*: δ = 0.00 (s, 6H, $2CH_3$), 0.80 (s, 9H, $C(CH_3)_3$), 2.23 (dd, J = 17.0, 4.9Hz, 1H, CH_2), 2.35 (dd, J = 14.3, 9.1Hz, 1H, CH_2), 2.45-2.55 (m, 1H, CH_2), 2.54 (dd, J = 17.0, 6.9Hz, 1H, CH_2), 3.67 (dt, J = 9.1, 4.4Hz, 1H, CHN), 4.05 (ddd, J = 6.9, 4.9, 4.2Hz, 1H, CHO), 5.16, 5.19 (2brs, 1H, $=CH_2$), 5.21, 5.22 (2d, J = 1.5Hz, 1H, $=CH_2$), 5.79 (brs, 1H, NH). ^{13}C NMR ($CDCl_3$, mixture of rotamers): *cis*: δ = -5.0 (1C), -4.6 (1C), 18.0 (1C), 25.7 (3C), 40.2 (0.5C), 40.3 (0.5C), 42.2 (1C), 56.9 (1C), 68.9 (0.5C), 69.0 (0.5C), 120.0 (0.5C), 120.1 (0.5C), 130.6 (1C), 174.8 (1C); *trans*: δ = -4.8 (1C), -4.6 (1C), 17.9 (1C), 25.6 (3C), 38.8 (0.5C), 40.1 (0.5C), 46.0 (1C), 61.2 (1C), 72.5 (0.5C), 72.6 (0.5C), 115.6 (0.5C), 115.6 (0.5C), 129.2 (1C), 174.9 (1C). MS (FAB, mNBA) m/z = 336.1, 334.1 (M^++H), 254.2 (M^+-Br). MS (70eV) m/z = 320, 318 (M^+-CH_3), 278, 276 (M^+-C_4H_9). HRMS calculated for $C_{12}H_{21}BrNO_2Si$ (M^+-CH_3) 318.0525, found 318.0523.

***cis*- and *trans*-(4*R*)-5-Allenyl-4-*tert*-butyldimethylsilyloxy-2-pyrrolidone (4f).** **4f** was synthesized according to method B using 0.35 ml of propargyltrimethylsilane as nucleophile. The minor *trans* diastereomer could not be isolated and characterized. Yield: 57 mg of **4f** (23%, ds (*cis*): 87%). Yellow oil (*cis*). R_f: 0.21 (*cis*) (EtOAc/cyclohexane 1:1). $[\alpha]_{25}^{D}$ = +18.6° (c = 0.75, EtOH) (*cis*). ^1H NMR ($CDCl_3$): *cis*: δ = 0.00 (s, 6H, $2CH_3$), 0.82 (s, 9H, $C(CH_3)_3$), 2.23 (dd, J = 16.7, 4.7Hz, 1H, CH_2), 2.45 (dd, J = 16.7, 6.2Hz, 1H, CH_2), 4.12 (dd, J = 6.9, 6.2Hz, 1H, CHN), 4.43 (td, J = 6.2, 4.7Hz, 1H, CHO), 4.77 (dd, J = 6.4, 2.0Hz,

1H, $=CH_2$), 4.78 (dd, J = 6.7, 2.0Hz, 1H, $=CH_2$), 5.18 (td, J = 6.9, 6.6Hz, 1H, =CH), 5.85 (brs, 1H, NH). ^{13}C NMR ($CDCl_3$): *cis*: δ = -4.9, -4.8, 18.1, 25.7, 39.9, 58.7, 70.1, 77.2, 88.3, 175.3, 208.6. MS (EI) m/z = 253.1 (M^+), 238.1 (M^+-CH_3), 196 (M^+-C_4H_9). HRMS calculated for $C_{13}H_{23}NO_2Si$ 253.1492, found 253.1503.

***cis*- and *trans*-(4*R*)-4-*tert*-Butyldimethylsilyloxy-5-cyano-2-pyrrolidone (4g).** **4g** was synthesized according to method A using 0.33 ml of trimethylsilylcyanide as nucleophile. The minor *trans* diastereomer could not be isolated and characterized. Yield: 131 mg of **4g** (55%, ds (*cis*): 77%). Mp: 148-150°C (white crystals, *cis*). R_f: 0.25 (*cis*) (EtOAc/cyclohexane 1:1). $[\alpha]_{25}^{D}$ = +19.1° (c = 1.03, EtOH) (*cis*). ^1H NMR ($CDCl_3$): *cis*: δ = 0.11, 0.13 (2s, 6H, $2CH_3$), 0.91 (s, 9H, $C(CH_3)_3$), 2.46 (dd, J = 16.7, 6.6Hz, 1H, CH_2), 2.58 (dd, J = 16.7, 6.9Hz, 1H, CH_2), 4.53 (d, J = 6.4Hz, 1H, CHN), 4.64 (q, J = 6.6Hz, 1H, CHO), 6.64 (brs, 1H, NH). ^{13}C NMR ($CDCl_3$): *cis*: δ = -5.0, -4.8, 18.0, 25.6, 38.4, 51.4, 68.1, 115.6, 174.3. HRMS calculated for $C_{11}H_{20}N_2O_2Si$ 240.1289, found 240.1291. Anal. found C, 54.59; H, 8.38; N, 11.31. Calculated for $C_{11}H_{20}N_2O_2Si$: C, 54.96; H, 8.39; N, 11.65.

***trans* - and *cis*-(4*R*)-5-Di(ethoxycarbonyl)methyl-4-*tert*-butyldimethylsilyloxy-2-pyrrolidone (4h).** **4h** was synthesized according to method C using 0.31 ml of malonic acid diethyl ester as nucleophile. Yield: 246 mg of **4h** (66%, ds (*trans*): 80%). Colorless oil (*cis* and *trans*). R_f: 0.33 (*cis*), 0.41 (*trans*) (EtOAc/cyclohexane 1:1). $[\alpha]_{25}^{D}$ = +4.1° (c = 1.14, EtOH) (*trans*), +12.3° (c = 1.5, EtOH) (*cis*). ^1H NMR ($CDCl_3$, mixture of rotamers): *trans*: δ = -0.01, 0.00 (2s, 6H, $2CH_3$), 0.80 (s, 9H, $C(CH_3)_3$), 1.19, 1.22 (2t, J = 7.1Hz, 6H, CH_3), 2.16 (dd, J = 17.2, 3.4Hz, 1H, CH_2), 2.55 (dd, J = 17.2, 6.6Hz, 1H, CH_2), 3.36 (d, J = 6.9Hz, 1H, CH), 3.89 (dd, J = 6.9, 2.7Hz, 1H, CHN), 4.14, 4.16 (2q, J = 7.1Hz, 2H, OCH_2), 4.34 (ddd, J = 6.4, 3.2, 2.9Hz, CHO), 6.08 (brs, 1H, NH); *cis*: δ = -0.06, 0.00 (2s, 6H, $2CH_3$), 0.80 (s, 9H, $C(CH_3)_3$), 1.21, 1.22 (2t, J = 7.1Hz, 6H, $2CH_3$), 2.22 (dd, J = 17.0, 3.0Hz, 1H, CH_2), 2.51 (dd, J = 17.0, 6.2Hz, 1H, CH_2), 3.68 (d, J = 10.1Hz, 1H, CH), 4.21 (dd, J = 10.1, 5.2Hz, 1H, CHN), 4.16, 4.22 (2q, J = 7.1Hz, 1H, OCH_2), 4.55 (td, J = 5.6, 3.0Hz, 1H, CHO), 6.14 (brs, 1H, NH). ^{13}C NMR ($CDCl_3$): *trans*: δ = -4.9, -4.7, 13.9, 14.0, 17.8, 25.6, 39.8, 54.7, 62.1, 62.2, 62.3, 70.2, 166.9, 167.2, 174.9; *cis*: δ = -5.3, -4.5, 13.9, 14.0, 17.9, 25.7, 40.3, 51.5, 57.8, 61.6, 62.2, 68.6, 73.3, 166.8, 168.5, 175.0. MS (EI) m/z = 374 (M^++H), 358 (M^+-CH_3), 316 (M^+-C_4H_9). Anal. found C, 54.39; H, 8.38; N, 3.80. Calculated for $C_{17}H_{31}NO_6Si$: C, 54.67; H, 8.36; N, 3.75.

***cis*- and *trans*-(4*R*)-5-(1-Methoxycarbonyl-2-oxo-propyl)-4-*tert*-butyldimethylsilyloxy-2-pyrrolidone (4i).** **4i** was synthesized according to method A using 0.39 ml of methyl 3-trimethylsiloxy-2-butenoate as nucleophile. Only the major 2,3-*cis*-diastereomer could be isolated and characterized as a 57:43 mixture of two diastereomers. Yield: 171 mg of **4i** (52%, ds (*cis*): 80%). Colorless oil (*cis*). R_f: 0.21 (*cis*), 0.27 (*trans*) (EtOAc/cyclohexane 1:1). ^1H NMR ($CDCl_3$): *cis (major diastereomer)*: δ = -0.00, 0.06 (2s, 6H, $2CH_3$), 0.86 (s, 9H, $C(CH_3)_3$), 2.27 (dd, J = 17.0, 4.9Hz, 1H, CH_2), 2.32 (s, 3H, CH_3), 2.53 (dd, J = 17.0, 3.4Hz, 1H, CH_2), 3.77 (s, 3H, OCH_3), 3.94 (d, J = 10.1Hz, 1H, CH), 4.41 (ddd, J = 10.1, 5.9, 0.7Hz, 1H, CHN), 4.58-4.62 (m, 1H, CHO), 6.31 (brs, 1H, NH); *cis (minor diastereomer)*: δ = 0.00, 0.06 (2s, 6H, $2CH_3$), 0.87 (s, 9H, $C(CH_3)_3$), 2.24 (dd, J = 17.0, 3.5Hz, 1H, CH_2), 2.34 (s, , 3H, CH_3), 2.57 (dd, J = 17.0, 3.0Hz, 1H, CH_2), 3.75 (s, 3H, OCH_3), 3.97 (d, J = 10.1Hz, 1H, CH), 4.35 (dd, J = 10.3, 5.4Hz, 1H, CHN), 4.58-4.62 (m, 1H, CHO), 6.22 (brs, 1H, NH). ^{13}C NMR ($CDCl_3$): *cis (major diastereomer)*: δ = -5.0, -4.8, 18.1, 25.8, 30.8, 39.7, 53.1, 57.7, 58.7, 68.5, 167.0, 174.7, 200.1; *cis (minor diastereomer)*: δ = -5.3, -4.5, 17.9, 25.7, 30.3, 40.1, 52.6,

57.4, 59.6, 68.6, 168.4, 175.3, 202.5. MS (FAB, mNBA) m/z = 330.2 (M^++H). MS (EI) m/z = 298.1 (M^+-OCH_3), 272 (M^+-C_4H_9). HRMS calculated for $C_{14}H_{24}NO_4Si$ (M^+-OCH_3) 298.1475, found 298.1475.

(4*R*)-4-*tert*-Butyldimethylsilyloxy-2-pyrrolidone (4j). **4j** was synthesized according to method A using 0.32 ml of triethylsilane as nucleophile. Yield: 80 mg of **4j** (37%). Mp: 80-82°C (white crystals). R_f: 0.28 (EtOAc/cyclohexane 1:1). $[\alpha]_{25}^D$ = +20.4° (c = 1.01, EtOH). ^{1}H NMR ($CDCl_3$): δ = -0.01, 0.00 (2s, 6H, $2CH_3$), 0.81 (s, 9H, $C(CH_3)_3$), 2.19 (dd, J = 17.0, 4.2Hz, 1H, CH_2), 2.47 (dd, J = 17.0, 6.9Hz, 1H, CH_2), 3.17 (dd, J = 10.1, 3.4Hz, 1H, CH_2N), 3.51 (dd, J = 10.1, 6.2Hz, 1H, CH_2N), 4.48 (tdd, J = 6.4, 3.9, 3.4Hz, 1H, CHO), 6.20 (brs, 1H, NH). ^{13}C NMR ($CDCl_3$): δ = -4.9, -4.8, 18.0, 25.7, 40.4, 51.6, 67.9, 176.4. MS (FAB, mNBA) m/z = 216.1 (M^++H). Anal. found C, 51.51; H, 9.85; N, 5.97. Calculated for $C_7H_{11}NO_2Si$ x H_2O: C, 51.46; H, 9.93; N, 6.00. The analytical data were identical with **4j** obtained by simple protection of starting material **1** in the form of the TBDMS ether. Optical rotation for this compound: $[\alpha]_{25}^D$ = +19.8° (c = 1.0, EtOH).

(4*R*,5*R*)-5-Allyl-4-hydroxy-2-pyrrolidone (5). To a solution of ***cis*-4a** (255 mg, 1 mmol) in 20 ml dry THF tetrabutylammonium fluoride in THF (1 M, 2.5 ml, 2.5 mmol) was added, and the mixture was stirred for 4 h. After evaporation of the solvent, purification by flash chromatography (EtOAc/EtOH 5:1) afforded a colorless oil which crystallized upon standing at 0°C to a white solid (141 mg, 100%). Mp: 55-57°C. R_f: 0.49 (EtOAc/EtOH 5:1). $[\alpha]_{25}^D$ = +29.7° (c = 0.7, EtOH). ^{1}H NMR (CD_3OD): δ = 2.09 (dd, J = 17.0, 2.5Hz, 1H, CH_2), 2.17 (ddt, J = 7.6, 6.4, 1.5Hz, 1H, CH_2), 2.32 (tt, J = 6.4, 1.5Hz, 1H, CH_2), 2.52 (dd, J = 17.0, 6.2Hz, 1H, CH_2), 3.55 (ddd, J = 7.6, 6.4, 4.9Hz, 1H, CHN), 4.26 (ddd, J = 6.2, 4.9, 2.5Hz, 1H, CHO), 4.97 (ddt, J = 10.1, 2.0, 1.2Hz, 1H, $=CH_2$), 5.04 (ddpt, J = 17.2, 2.0, 1.5Hz, 1H, $=CH_2$), 5.76 (ddpt, J = 17.2, 10.1, 6.4Hz, 1H, =CH). ^{13}C NMR (CD_3OD): δ = 34.7, 41.8, 60.9, 69.2, 118.1, 135.9, 178.8. HRMS calculated for $C_7H_{11}NO_2Si$ 141.0787, found 141.0784.

(4*R*,5*R*)-5-Allyl-4-methanesulfoxy-2-pyrrolidone (6). To a solution of **5** (141 mg, 1mmol) in 10 ml CH_2Cl_2 were added at 0°C methanesulfonyl chloride (83 µl, 1.1 mmol) and triethylamine (183 µl, 1.3 mmol).The solution was stirred at 0°C for 1 h, and was then allowed to warm to rt. After stirring overnight , water was added and the mixture was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. Flash chromatography (EtOAc/EtOH 5:1) afforded **6** as a white solid (191 mg, 87%). Mp: 86-88°C. R_f: 0.59 (EtOAc/EtOH 5:1). $[\alpha]_{25}^D$ = +3.6° (c = 1.1, EtOH). ^{1}H NMR (CD_3OD): δ = 2.34 (ddd, J = 14.3, 9.1, 8.4Hz, 1H, CH_2), 2.52 (ddddd, J = 14.3, 5.3, 5.0, 2.5, 1.5Hz, 1H, CH_2), 2.67 (dd, J = 17.7, 2.5Hz, 1H, CH_2), 2.80 (dd, J = 17.7, 6.4Hz, 1H, CH_2), 3.08 (s, 3H, SCH_3), 3.93 (dt, J = 9.4, 4.9Hz, 1H, CHN), 5.21 (ddd, J = 10.5, 2.7, 1.5Hz, 1H, $=CH_2$), 5.23 (ddd, J = 17.2, 2.7, 1.5Hz, 1H, $=CH_2$), 5.34 (td, J = 5.7, 2.5Hz, 1H, CHO), 5.80 (dddd, J = 16.9, 10.3, 8.2, 5.7Hz, 1H, =CH), 6.07 (brs, 1H, NH). ^{13}C NMR (CD_3OD): δ = 34.2, 38.7, 38.8, 57.9, 76.2, 119.4, 132.7, 174.2. MS (EI) m/z = 220 (M^++H), 178 (M^+-C_3H_7), 140 (M^+-CH_3SO_2). HRMS calculated for $C_5H_8NO_4S$ (M^+-C_3H_7) 178.0172, found 178.0177, calculated for $C_7H_{10}NO_2$ (M^+-CH_3SO_2) 140.0709, found 140.0712.

Crystal Structure Analysis of 6: A colorless crystal of **6** with the dimensions 0.40 x 0.30 x 0.20 was obtained by dissolving this substance in dichloromethane. The crystal was measured on a CAD 4 diffractometer using CuK_α radiation (λ = 1.54178 Å). Crystal data: $C_8H_{13}N_4S$, M = 219.25 g/mol,

orthorhombic space group P 2(1) 2(1) 2(1), a = 6.795(1) Å, b = 10.603(2) Å, c= 14.476(3) Å, V = 1043.0(3) $Å^3$, Z = 4, D_c= 1.396 g/cm^3, F (464), μ (CuK_α) = 0.272 mm^{-1}. At 295 (2) K in the range of 5.17° < θ < 65.81° 967 reflections were measured with $R_1[I>2\sigma(I)]$ = 0.0399, wR_2 (F^2) = 0.0993 and Goof = 1.011. The structure was solved by direct methods and refined by least squares procedure within the SHELX program system.

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14. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.