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Asymmetric [2,3]-Sigmatropic Wittig Rearrangement of Chiral α-Allyloxy-Hydrazones

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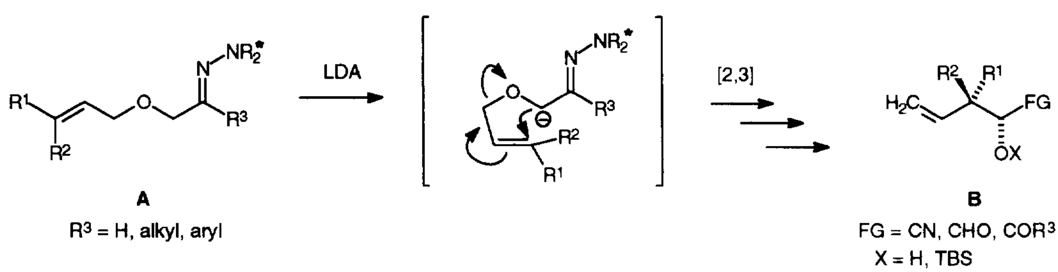
Abstract: The asymmetric [2,3]-Wittig rearrangement of chiral α-allyloxy-hydrazones (*S*)-**3** and (*S*)-**7** proceeds with very good yields (72 - 100%) together with high *syn*-selectivities (87 - 97%) and asymmetric inductions (63 - 92%) to give the corresponding α-hydroxyhydrazones **4** and **8**. Depending on the substitution patterns of the starting material, optically active aliphatic and aromatic α-hydroxyketones **5** or protected cyanohydrins **10** and α-hydroxyaldehydes **11** respectively, can be generated in high enantiomeric excesses (92 - 98%) and *syn*-selectivities (88 - >99%) after chromatographic purification and removal of the auxiliary.

The [2,3]-Wittig rearrangement involves the isomerisation of α-metalated allyl ethers to afford their corresponding homoallylic alcohols[1]. Since its first discovery by Wittig[2] and the proof of its cyclic mechanism by Schöllkopf[3] the [2,3]-Wittig rearrangement has become a powerful synthetic method in organic chemistry[1]. Because of the concerted mechanism involving a five-membered, envelope-like transition state, the reaction often proceeds with high stereoselectivities which have been rationalized by steric effects and electronic interactions[4]. Consequently numerous applications in natural product synthesis have been reported[1,5].

Asymmetric versions of the [2,3]-sigmatropic Wittig-rearrangement often start from optically active allylic alcohols and give enantiomerically enriched products *via* chirality transfer[1,6]. Enantioselective variants have been reported by Marshall[7] and Nakai[8] and asymmetric inductions with retention of the directing centre have been achieved with substituents in the allyl group[9] or by a chiral auxiliary attached to the carbanionic moiety of the molecule[10]. Along these lines we have recently reported the asymmetric [2,3]-Wittig rearrangement of chiral α-allyloxyacetaldehyde-hydrazones for the diastereo- and enantioselective synthesis of protected β-substituted, γ,δ-unsaturated α-hydroxyaldehydes and cyanohydrins[11] and the extension of this methodology to the auxiliary-controlled rearrangement of chiral α-allyloxyketone-hydrazones[12].

We now wish to report in full our investigations into the asymmetric [2,3]-Wittig rearrangement of α-allyloxy-hydrazones **A** allowing the diastereo- and enantioselective synthesis of protected cyanohydrins

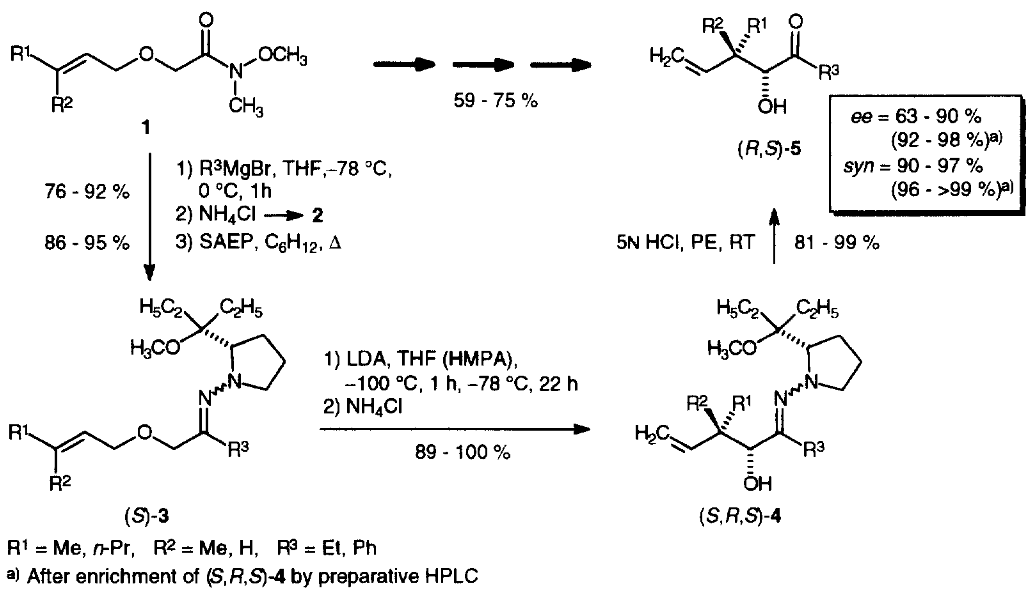


Scheme 1. Asymmetric [2,3]-Wittig rearrangement of α-allyloxy-hydrazones **A** to form cyanohydrins, α-hydroxyaldehydes and α-hydroxyketones **B**

and α-hydroxyaldehydes as well as aromatic and aliphatic α-hydroxyketones **B** with variable substituents in β-position. These optically active α-hydroxycarbonyl compounds are of special interest as versatile building blocks in organic synthesis and many efforts have been made for their stereoselective synthesis[11,12,13].

For the flexible synthesis of aromatic and aliphatic ketone-hydrazones (*S*)-**3**, (*E*)-configurated allyloxyacetamides **1** were synthesised in two or three steps starting from the corresponding allylic alcohols. Addition of aliphatic and aromatic Grignard reagents according to literature procedures[14] and purification by distillation or column chromatography afforded the allyloxyketones **2** in good yields (76 - 92%). After condensation with (*S*)-1-amino-2-(1-ethyl-1-methoxypropyl)pyrrolidine (SAEP)[15] the hydrazones (*S*)-**3** were obtained in good overall yields (65 - 87%) as mixtures of (*E*/*Z*) isomers at the C=N double bond but (*E*)-selective concerning the C=C double bond [except (*S*)-**3b**, $R^1 = R^2$ = Me].

For [2,3]-Wittig rearrangement the hydrazones (*S*)-**3** were metalated with lithium diisopropylamide at low temperature and gave the α-hydroxyhydrazones (*S*,*R*,*S*)-**4** as (*E*/*Z*) isomers in good to quantitative yields (89 - 100%) after purification by column chromatography. Cleavage of the chiral auxiliary was achieved simply by stirring the hydrazones **4** with 5N HCl in light petroleum until no hydrazone could be detected by TLC. Purification by column chromatography afforded the α-hydroxyketones (*R*,*S*)-**5** in good to nearly quan-titative yields (81 - 99%) together with excellent *syn*/*anti*-selectivities (90 - 97% *syn*) and high enantiomeric excesses (63 - 90% *ee*). Interestingly, hexamethylphosphoric triamide (HMPA) as cosolvent is essential to achieve good selectivities for the rearrangement of aliphatic ketone-hydrazones (**5c**, *syn* = 93%, *ee* = 84% with HMPA; *syn* = 91%, *ee* = 29% without HMPA), whereas it diminishes the asymmetric inductions for the rearrangement of aromatic hydrazones (**5e**, *syn* = 94%, *ee* = 90% without HMPA; *syn* = 96%, *ee* = 47% with HMPA). By enrichment of the major diastereomer of **4** by HPLC before cleavage, α-hydroxyketones of very high enantiomeric and diastereomeric purity could be obtained (94 - > 99% *syn*, 92 - 98% *ee*).



Scheme 2. Asymmetric synthesis of α-hydroxyketones by [2,3]-Wittig rearrangement of SAEP hydrazones

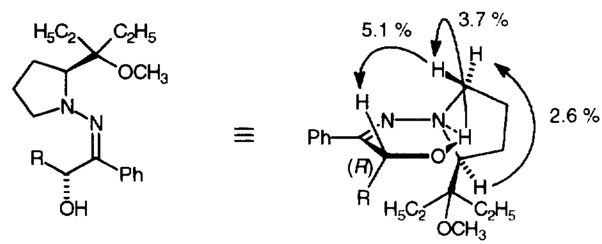
The *syn*-configuration of the newly created stereogenic centres could be assigned by ^1H NMR NOE measurements of α-hydroxyketones **5c** and **5e** and the ratios were determined by GC or ^1H NMR spectroscopy.

Table 1. Optically Active α-Hydroxyketones **5** by [2,3]-Wittig Rearrangement of Ketone-Hydrazones **3**.

5	R¹	R²	R³	yield 1→2 [%]	yield 2→3 [%]	yield 3→4 [%]	yield 4→5 [%]	$[\alpha]_D^{RT}$ (c, $CHCl_3$)	*syn*[a] [%]	*ee*[a,b] [%]	(config.)
a	Me	H	Et	89	86	94	81	−148.4 (1.0)	97 (>99)[c]	81 (96)	(*R,S*)
b	Me	Me	Et	92	95	92	88	−152.7 (1.0)	—	63 (92)	(*R*)
c	*n*-Pr	H	Et	85	95	89	92	−119.6 (1.3)	93 (97)[d]	84 (98)	(*R,S*)
d	Me	H	Ph	76	95	98	98	−17.0 (1.3)	90 (98)[c]	90 (92)	(*R,S*)
e	*n*-Pr	H	Ph	76	86	100	99	−51.0 (1.2)	94 (96)[d]	90 (93)[e]	(*R,S*)

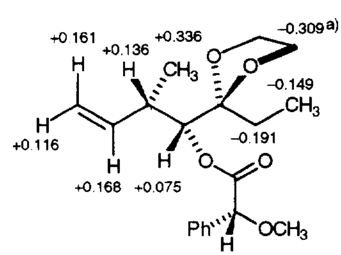
[a] In parantheses: after HPLC of **4** (Merck, prepared column, silica gel 7μ, length 250 mm, diethyl ether/ light petroleum; [b] determined by ^1H NMR spectroscopy using (−)-(*R*)-1-(9-anthryl)-2,2,2-trifluoroethanol[16] as chiral cosolvent; [c] determined by gas chromatography; [d] determined by ^1H NMR spectroscopy; [e] determined by gas chromatography with a permethylated cyclodextrine phase and HPLC employing a chiral stationary phase (Chiracel).

The absolute configuration of the rearranged products could be deduced from ^1H NMR measurements of α-hydroxyhydrazone **5d**. The (*E*) and (*Z*) isomers were separated by HPLC and the (*Z*) isomer was shown to possess a rigid hydrogen-bridged conformation as is depicted in scheme 2. From NOE experiments the configuration of the new stereogenic centre can be predicted relative to the pyrrolidine center of known (*S*)-



5d

R = $CH(CH_3)CH{=}CH_2$



(*R,R,S*)-**6**

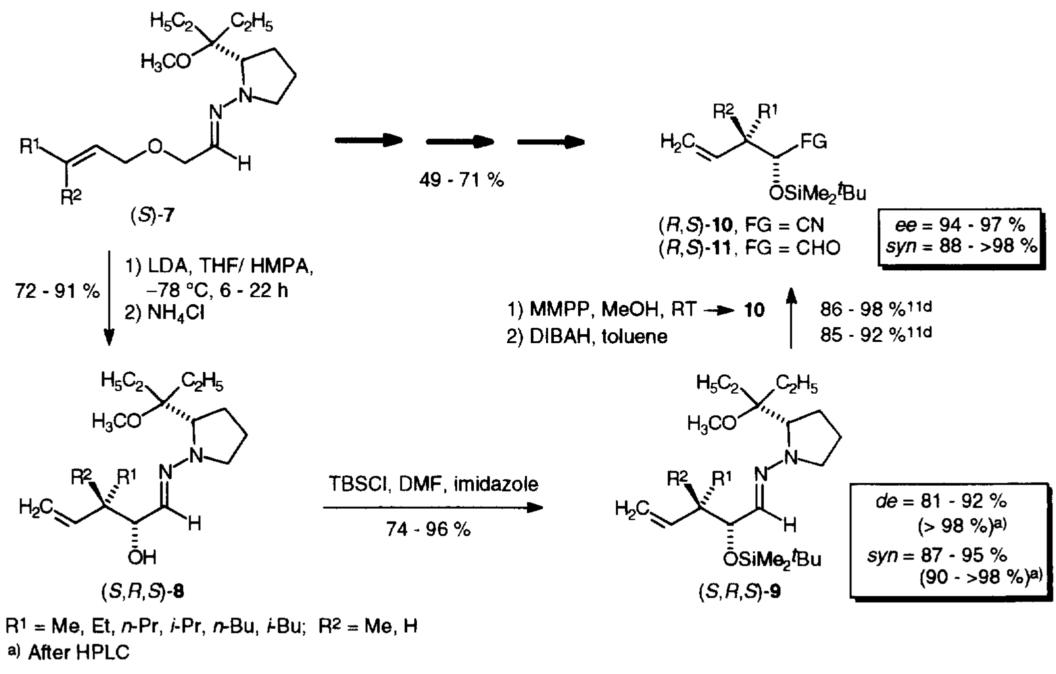
The arrows, which stand for the observed NOE effects point from the irradiated to the observed signal; data of the relative enhancements are given in percentages.

The differences in the ^1H NMR shifts of (*R,R,S*)-**6** and (*S,R,S*)-**6** [Δδ = δ(*R*) − δ(*S*)] at 500 MHz are given; [a] average value of the four ring protons.

Scheme 3. Determination of the absolute configuration by ^1H NMR measurements configuration and therefore has to be (*R*), hence the absolute configuration of **4d** is *syn*-(2*R*,3*S*). This absolute configuration could be confirmed for ketone **5a** by analysis of the chemical shift differences in the ^{1}H NMR spectrum of (*R*)- and (*S*)-α-methoxyphenylacetates **6a** according the modified Mosher's method[12,17] (scheme 2). Protection of the carbonylfunctionality was necessary before esterification because otherwise the elimination product (3-methyl-hepta-4,6-dien-3-one) was isolated.

The α-allyloxyacetaldehyde-SAEP hydrazones (*S*)-**7** are available from the corresponding allyloxyacetaldehydes[18] by condensation with SAEP. Purification by column chromatography afforded the hydrazones as (*E*) isomers at the C=N bond with ≤ 5% of the $(Z)_{CC}$ isomer. As is depicted in scheme 3, metalation with LDA at low temperature in THF/HMPA and purification by column chromatography afforded the products of the [2,3]-Wittig rearrangement (*S*,*R*,*S*)-**8** in good yields (72 - 91%) as pale yellow liquids. The *syn*-selectivities are high (*syn* = 87 - 95%) with decreasing tendency for increasing steric bulk of R^1 (table 2), whereas the asymmetric inductions are generally high (*de* = 90 - 92%) with the exception of the rearrangement of prenylether **7b** (*de* = 81%). From rearrangement of (*Z*)-but-2-enyloxyacetaldehyde-SAEP hydrazone[19] [92% $(Z)_{CC}$] the *anti*-configurated product was isolated with significantly lower selectivities (*syn*/*anti* = 31/69; de_{syn} = 84%, de_{anti} = 28%), which corresponds to the findings for other enolate [2,3]-Wittig processes[1].

Silylation with *tert*-butyldimethylsilyl chloride (TBSCl) in dimethylformamide (DMF) and purification by column chromatography on deactivated silica gel delivered the protected hydrazones (*S*,*R*,*S*)-**9** in good to very good yields (74 - 96%) with no change in isomer ratios. By the use of preparative HPLC, the diastereomeric excesses could be increased to >98%, while the *syn*/*anti*-proportions enhanced to 90 - >98%



Scheme 4. Optically active protected α-hydroxyaldehydes and cyanohydrins by [2,3]-Wittig rearrangement

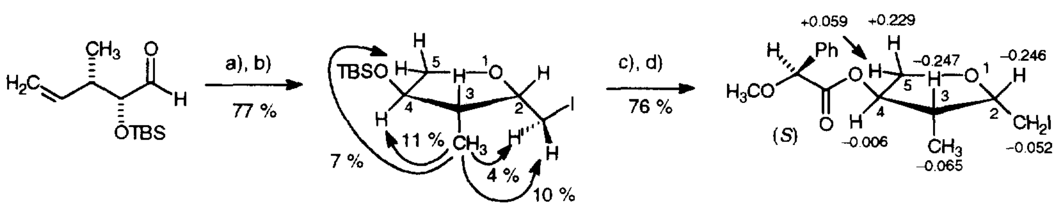
(table 2). As previously reported[11], the α-silyloxyhydrazones **9** could readily be converted to protected cyanohydrins (*R*,*S*)-**10** by magnesium monoperoxyphthalate (MMPP) mediated oxidation. Subsequent reduction with DIBAH[20] afforded the protected, β-substituted, γ,δ-unsaturated α-hydroxyaldehydes (*R*,*S*)-**11**. This process allows the synthesis of both classes of compounds with high *syn*-selectivities (*syn* = 88 - >98%) and enantiomeric excesses (*ee* = 94 - 97%) in good to very good overall yields (49 - 71%) starting from hydrazones (*S*)-**7**.

Table 2. Asymmetric [2,3]-Wittig Rearrangement of α-Allyloxyaldehyde-SAEP Hydrazones **7** to α-Hydroxyaldehyde Hydrazones **8** and **9**.

9	R^1	R^2	yield 7→8 [%]	yield 8→9 [%]	$[\alpha]_D^{RT}$ (*c*, $CHCl_3$)	*syn*[a)] [%]	*de*[a)] [%]	(config.)
a	Me	H	86	93	+32.6 (1.0)	95 (>98)	91 (> 98)	(*S*,*R*,*S*)
b	Me	Me	72	94	+11.3 (1.0)	—	81 (>98)	(*S*,*R*)
c	Et	H	81	92	+49.3 (1.2)	92 (93)	92 (>98)	(*S*,*R*,*S*)
d	*n*-Pr	H	91	93	+46.0 (1.1)	92 (93)	92 (>98)	(*S*,*R*,*S*)
e	*i*-Pr	H	91	96	+67.6 (1.0)	87 (90)	91 (>98)	(*S*,*R*,*S*)
f	*n*-Bu	H	89	91	+46.9 (1.0)	90 (96)	90 (>98)	(*S*,*R*,*S*)
g	*i*-Bu	H	81	74	+56.5 (1.0)	88 (98)	90 (>98)	(*S*,*R*,*S*)

a) Determined by ^{13}C NMR spectroscopy of **9** (75 MHz, 2 h); In paranthesis values after purification of **9** by HPLC.

In order to determine the relative configuration of the rearrangement products, aldehyde **11a** was reduced with $NaBH_4$ and cyclised by iodoetherification[21]. Purification by column chromatography furnished the trisubstituted tetrahydrofuran **12** as a mixture of two diastereomers (73/27) in good overall yield (77%).



(2*R*,3*S*)-**11a**

TBS = $SiMe_2{}^tBu$

2,3-*cis*-3,4-*trans*-**12**, 73 %
+
2,3-*trans*-2,4-*trans*-**12**, 27 %

(*S*)-**13**

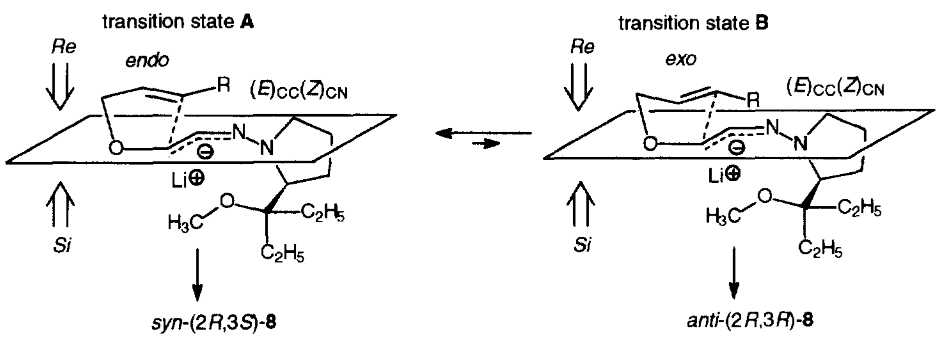
The arrows stand for the observed NOE effects, point from the irradiated to the observed signal, data of the relative increases in intensity are given; the differences in the ^1H NMR shifts of (*S*)-**13** and (*R*)-**13** [$\Delta\delta = \delta(S) - \delta(R)$ at 500 MHz) are given; a) $NaBH_4$, MeOH, 0 °C, 1 h; b) I_2, $NaHCO_3$, Et_2O/H_2O (5/2), RT, 18 h; MeOH, HCl, 0 °C, 1 h; d) (*S*)- or (*R*)-MPA, DMAP, DCC, CH_2Cl_2, RT, 18 h.

Scheme 5. Determination of the absolute configuration for aldehyde **11a**.

As is depicted in scheme 4, the NOE effects from irradiation of the methyl-signal proved a 2,3-*cis*-3,4-*trans*-configuration for the predominant isomer, which means a *syn*-configuration for aldehyde **11a**. Although no efforts were made to further enhance the selectivity of the iodoetherification, this process shows a flexible entry to optically active trisubstituted tetrahydrofurans which are of synthetic interest[21,22].

The absolute configuration was deduced from ^1H NMR analysis of esters (*S*)-**13** and (*R*)-**13** synthesised by desilylation of **12** and subsequent esterification with (*R*)- and (*S*)-α-methoxyphenylacetic acid (MPA). As can be seen from scheme 4, the methine signals at C-2 and C-3 are significantly high field shifted (–0.247 ppm, –0.246 ppm) for the (*S*)-MPA ester with respect to the corresponding (*R*)-MPA ester while the methyl signals for C-5 appear at lower field (+0.229 ppm, +0.059 ppm). This indicates a (*S*)-configuration at C-4 so that the absolute configuration of aldehyde **11a** can be predicted as *syn*-(2*R*,3*S*). The total synthesis of naturally occurring (–)-oudemansin A[5f] confirmed the (*R*,*S*)-configuration and demonstrated the synthetic value of this [2,3]-sigmatropic process.

The stereochemical trends observed in the rearrangement of **3** and **7** can be rationalised in terms of the transition states **A** and **B** (scheme 5). The 1-aza-allylanion formed after deprotonation with lithium diisopropylamide should possess a $(E)_{CC}(Z)_{CN}$-configuration as shown by earlier investigations[23] and could be proved by isolation of a $(Z)_{CN}$-configurated rearrangement product from **7b** after work up at low temperature. In contrast to the normally observed *Si*-attack of electrophiles[23], the allylic part should occupy the *Re*-orientation (with respect to the reaction centre) as the *Si*-side is sterically shielded by the pyrrolidine subsituent. This assumption is confirmed by the observation that the sterically less demanding (*S*)-1-amino-2-methoxymethylpyrrolidine (SAMP) gave significantly lower asymmetric inductions (57 % *de*, for the hydrazone analogous to **7a**). On the basis of *ab initio* calculations for the [2,3]-Wittig rearrangement of the closely related allyloxyacetaldehyde enolates by Houk[4d], an *endo*-conformation of the five-membered transition state should be favoured leading to *syn*-(2*R*,3*S*)-configurated products (scheme 5), while the disfavoured *exo*-transition state furnishes *anti*-(2*R*,3*R*)-configurated products. This transition state model is also applicable to the rearrangement of α-allyloxyketone hydrazones **3** as products of the same absolute configuration are formed, independent from the use of cosolvents.



Scheme 6. Transition state models for the [2,3]-Wittig rearrangement of α-allyloxy-SAEP hydrazones

In conclusion, the asymmetric [2,3]-Wittig rearrangement of SAEP hydrazones (*S*)-**3** and (*S*)-**7** described here offers an efficient entry to γ,δ-unsaturated α-hydroxyketones, -aldehydes and cyanohydrins with variable substitution in β-position and high *syn*-selectivities and enantiomeric excesses, starting from readily available precursors. As an extension of this work we are now investigating the auxiliary-controlled rearrangement of cyclic hydrazones and the stereoselective synthesis of allenes.

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EXPERIMENTAL

General. Metalation reactions were carried out using standard Schlenk techniques under an argon atmosphere. Solvents were dried and purified by conventional methods prior to use. Toluene was freshly distilled from sodium, tetrahydrofuran (THF) from potassium under argon. Light petroleum refers to the fraction with b.p. 40 - 80 °C. Reagents of commercial quality were used from freshly opened containers unless otherwise stated. *n*-Buthyllithium (1.6 M in *n*-hexane) was purchased from Merck.

The cyanohydrins **10** and α-hydroxyaldehydes **11** were prepared according to literature procedures[11], the allyloxyacetaldehydes were prepared from the allylic alcohols by standard procedures[18].

Apparatus. TLC: Merck glass-backed silica gel 60 F_{254} plates. - Preparative column chromatography: Merck silica gel 60, partical size 0.040 - 0.063 mm (230 - 400 mesh) (flash). - Analytical GC: Siemens Sichromat 2 or 3 equipped with a SE-54-CB-column (25 m x 0.25 mm) and SE-30-column (50 m x 0.25 mm) and a OV-1-CB-column (25 m x 0.2 mm), carrier gas nitrogen, FID. - Optical rotations: Perkin-Elmer P 241 polarimeter; solvents of Merck UVASOL quality. - IR spectra: Perkin-Elmer 1420 and Perkin-Elmer FT/IR 1750. - ^{1}H NMR spectra (300 and 500 MHz), ^{13}C NMR spectra (75 and 125 MHz): Varian VXR 300, Varian VXR 500 and Gemini 300 (solvent: $CDCl_3$, TMS as internal standard). - Mass spectra: Varian MAT 212 (EI 70 eV) (relative intensities in paranthesis). - GC-MS: GC: Varian 3700, FS 15-column (25 m x 0.25 mm); MS: Varian MAT 212 (EI 70 eV) (relative intensities in paranthesis). - HRMS: Finnigan MAT, MAT 95. - Preparative HPLC: Gilson, UV detector equipped with a Merck Lichrosorb Si60-column (250 mm x 25 mm). - Analytical HPLC: Hewlett Packard 1050, DAD detector equipped with a Daicel OD-column (250 mm x 4.6 mm).

General procedure for the preparation of α-allyloxyketones ***2:*** A solution of the corresponding amide **1** (10 mmol) in THF (30 ml) was cooled to –78 °C. A suspension of Grignard reagent (30 mmol EtMgBr or 50 mmol PhMgBr) in THF (20 ml) was added and the reaction mixture was hydrolysed by addition of 3 N HCl (100 ml) after stirring at 0 °C for 1 h. The solution was transfered to a separating funnel and extracted three times with CH_2Cl_2/ diethyl ether (1/ 1, 50 ml). The combined organic extracts were washed until neutral with brine and dried over $MgSO_4$. Evaporation of the solvent and purification by column chromatography or distillation afforded the pure ketones **2** as colourless liquids.

General procedure for the preparation of ketone hydrazones ***3:*** The corresponding ketone **2** (10 mmol) and SAEP (11 mmol) were dissolved in cyclohexane and heated to reflux with azeotrope water removal by a Dean Stark trap until the starting ketone had been completely converted (TLC control). Removal of the solvent under reduced pressure and purification by column chromatography (aromatic hydrazones) or distillation (aliphatic hydrazones) gave the pure hydrazones as pale yellow liquids.

General procedure for the preparation of aldehyde hydrazones 7: The corresponding allyloxyacetaldehyde[18] (11 mmol) was added dropwise at 0 °C to SAEP (10 mmol) and stirred at room temp. overnight. The mixture was diluted with diethyl ether (100 ml) and washed once with water (10 ml). Drying over $MgSO_4$, evaporation of the solvent and purification by column chromatography afforded hydrazones **7** as colourless to pale yellow liquids.

General procedure for the [2,3]-Wittig rearrangement to α-hydroxyhydrazones 4 and 8: A solution of diisopropylamine (2.8 mmol for aldehyde hydrazones/ 3.3 mmol for ketone hydrazones) in THF was treated with *n*-butyllithium (2.5 mmol/ 3.0 mmol) at 0 °C. After stirring for 15 min the solvent was removed under reduced pressure and the residue dissolved in THF (5 ml/ 15ml) together with HMPA (1 ml for **8**/ 3 ml for **4a-c**/ no HMPA for **4d,e**). The solution was cooled to –78 °C (**8**) or –100 °C respectively (**4**) and the corresponding hydrazone (1 mmol), diluted in THF (2 ml) was added dropwise. The aldehyde hydrazones were stirred at that temperature for 22 h and hydrolysed by addition of saturated NH_4Cl solution (20 ml) (for **4b**, stirring at –78 °C for 6 h, then 15 min at 0 °C). The ketone hydrazones are kept at –100 °C for 1 h followed by stirring at –78 °C (22 h, for **4a-c** additional stirring at 0 °C for 1h) before hydrolysis with saturated NH_4Cl solution. The mixture was diluted with diethyl ether (100 ml) and the organic phases washed twice with water (20 ml). The aqueous phases were extracted several times with diethyl ether and the combined organic extracts were dried over $MgSO_4$. Evaporation of the solvent and purification by column chromatography afforded the rearrangement products as pale yellow liquids.

General procedure for the preparation of α-silyloxyhydrazones 9: The silylation was achieved according to literature procedure[24] using 2.4 equiv. of TBSCl and 3 equiv. of imidazole. Purification by column chromatography on deactivated silica gel yielded the hydrazones **9** as colourless to pale yellow liquids.

General procedure for the synthesis of α-hydroxyketones 5: The ketone hydrazone **4** was dissolved in light petroleum at 0 °C and 5 N HCl (4 ml) was added with vigorous stirring. After additional stirring until the starting hydrazone had been completely converted (TLC control) the mixture was diluted with light petroleum (100 ml) and the aqueous phase was thoroughly seperated (additional washing of the organic phase with 3 N HCl) and the organic phase washed until neutral and dried over $MgSO_4$. After evaporation of the solvent the residue was purified by column chromatography yielding the pure products as a colourless liquid.

(E)-2-(But-2-enyloxy)-N-methoxy-N-methyl-acetamide (**1a**): Following a literature procedure[25] (*E*)-but-2-enyloxyacetic acid (78% yield, b.p. 60 - 65 °C/ 0.5 mbar) was synthesised from (*E*)-crotylic alcohol (0.32 mol) by deprotonation with NaH (1.1 mol) and etherification with bromoacetic acid (0.33 mol). The acid (0.20 mol) was dissolved in THF (800 ml) and stirred with 1,1-carbonyldiimidazole (CDI, 0.21 mol) until the evolution of CO_2 had stopped. After addition of *N,O*-dimethylhydroxylamine hydrochloride (0.21 mol) the suspension was stirred at room temp. for 2 days and filtered. The filtrate was diluted with diethyl ether and the resulting emulsion washed twice with 1 N H_2SO_4 and then brine. After drying over $MgSO_4$ the solvent was evaporated and the crude product purified by distillation affording the pure amide **1a** (75% yield) as a colourless liquid. - b.p. 55 - 60 °C/ 0.5 mbar. - IR (film): ν = 1684 (s, C=O), 1091 (s, COC) cm^{-1}. - ^1H NMR (300 MHz): δ = 1.73 (dd, *J* = 6.1 Hz/ 1.3 Hz, 3H, $CHCH_3$), 3.19 (s, 3H, NCH_3), 3.69 (s, 3H, OCH_3), 4.04 (dt, *J* = 6.4 Hz/ 1.0 Hz, 2H, $CHCH_2O$), 4.24 (s, 2H, OCH_2CO), 5.61 (m, 1H, $CHCH_2O$), 5.75 (m, 1H, $CHCH_3$) ppm. - ^{13}C NMR (75 MHz): δ = 17.52, 32.35, 61.45, 66.79, 71.99, 127.09, 130.37, 171.14 ppm. - GC/MS (70 eV)

m/z (%) = 103 (18, $OCH_2CONOCH_3^+$), 55 (100, $CH_3HCCHCH_2^+$). - $C_8H_{15}NO_3$ (173.2): calcd. C = 55.47, H 8.73, N 8.09; found C 55.77, H 8.94, N 8.46.

2-(3-Methyl-but-2-enyloxy)-N-methoxy-N-methyl-acetamide (**1b**): Following the procedure described above (3-methyl-but-2-enyloxy)acetic acid was synthesised from 3-methyl-but-2-enol (79% yield, b.p. 70 °C/ 0.5 mbar) and transformed to the corresponding amide. - 82% Yield. - b.p. 55 - 60 °C/ 0.1 mbar. - IR (film): ν = 1685 (s, C=O), 1085 (s, COC) cm^{-1}. - ^1H NMR (300 MHz): δ = 1.70 [s, 3H, $(CH_3)_{cis}$], 1.76 [s, 3H, $(CH_3)_{trans}$], 3.19 (s, 3H, NCH_3), 3.69 (s, 3H, OCH_3), 4.11 (d, *J* = 7.0 Hz, 2H, $CHCH_2O$), 4.25 (s, 3H, OCH_2CO), 5.39 (m, 1H, CH) ppm. - ^{13}C NMR (75 MHz): δ = 18.06, 25.81,32.37 , 61.40, 66.94, 67.66, 120.58, 137.89, 171.39 ppm. - GC/MS (70 eV): *m/z* (%) = 103 (74, $OCH_2CONOCH_3^+$), 69 (100, $(CH_3)_2CCHCH_2^+$). - $C_9H_{17}NO_3$ (187.2): calcd. C = 57.73, H 9.15, N 7.48; found C 57.77, H 9.14, N 7.54.

(E)-2-(Hex-2-enyloxy)-N-methoxy-N-methyl-acetamide (**1c**): Following the procedure described above (*E*)-2-(hex-2-enyloxy)acetic acid was synthesised from (*E*)-hex-2-enol (91 yield, b.p. 72 - 82°C °C/ 0.4 mbar), converted to the corresponding acid chloride with $SOCl_2$ according to standard procedures and transformed to the corresponding amide **1c** by reaction with *N,O*-dimethylhydroxylamine hydrochloride[13]. - 38% Yield from (*E*)-2-(hex-2-enyloxy)acetic acid. - b.p. 63 - 72 °C/ 0.01 mbar. - IR (film): ν = 1686 (s, C=O), 1084 (s, COC) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.90 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 1.41 (m, 2H, $CHCH_2CH_2$), 2.03 (m, 2H, $CHCH_2CH_2$), 3.19 (s, 3H, NCH_3), 3.69 (s, 3H, $NOCH_3$), 4.07 (dd, *J* = 6.7 Hz/ 1.1 Hz, 2H, $CHCH_2O$), 4.25 (s, 2H, OCH_2CO), 5.58 (m, 1H, $CHCH_2O$), 5.73 (m, 1H, $CHCH_2CH_3$) ppm. - ^{13}C NMR (75 MHz): δ = 13.67, 22.19, 32.36, 34.35, 61.45, 66.71, 72.09, 125.87, 135.59, 171.19 ppm. - GC/MS (70 eV): *m/z* (%) = 103 (68, $OCH_2CONOCH_3^+$), 83 (43, [*n*-Pr)$HCCHCH_2^+$]. - $C_{10}H_{19}NO_3$ (201.3): calcd. C 59.68, H 9.51, N 6.96; found C 59.39, H 9.76, N 6.71.

(E)-1-(But-2-enyloxy)-butan-2-one[26] (**2a**): 89% Yield from amide **1a** after distillation (b.p. 60 - 65 °C/ 13 mbar). - IR (film): ν = 1719 (s, C=O), 1671 (w, C=C), 1106 (s, COC) cm^{-1}. - ^1H NMR (300 MHz): δ = 1.07 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 1.71 (dd, *J* = 6.2 Hz/ 1.2 Hz, 3H, $CHCH_3$), 2.50 (q, *J* = 7.4 Hz, 2H, CH_2CH_3), 3.97 (m, 2H, $CHCH_2O$), 4.03 (s, 2H, OCH_2CO), 5.57 (dtq, *J* = 15.1 Hz/ 6.4 Hz/ 1.7 Hz, 1H, $CHCH_2O$), 5.75 (dqt, *J* = 15.4 Hz/ 6.4 Hz/ 1.3 Hz, 1H, $CHCH_3$) ppm. - ^{13}C NMR (75 MHz): δ = 7.26, 17.75, 32.23, 72.10, 74.54, 126.80, 130.62, 209.67 ppm. - GC/MS: (70 eV): *m/z* = 57 (80, $C_2H_5CO^+$), 55 (100, $C_4H_7^+$).

1-(3-Methyl-but-2-enyloxy)-butan-2-one (**2b**): 92% Yield from amide **1b** after distillation (b.p. 77 - 81 °C/ 12 mbar). - IR (film): ν = 1719 (s, CO), 1675 (w, C=C), 1101 (s, COC) cm^{-1}. - ^1H NMR (300 MHz): δ = 1.07 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 1.69 [d, *J* = 1.0 Hz, 3H, $(CH_3)_{cis}$], 1.76 [d, *J* = 1.0 Hz, 3H, $(CH_3)_{trans}$], 2.49 (q, *J* = 7.4 Hz, 2H, CH_2CH_3), 4.03 (s, 3H, OCH_2CO), 4.04 (d, *J* = 7.0 Hz, 2H, $CHCH_2O$), 5.35 (m, 1H, CH) ppm. - ^{13}C NMR (75 MHz): δ = 7.28, 18.04, 25.81, 31.18, 67.71, 74.66, 120.35, 138.14, 209.82 ppm. - GC/MS (70 eV): *m/z* (%) = 85 (79, [$(CH_3)_2CCHCH_2O^+$], 57 (48, $C_2H_5CO^+$). - $C_9H_{16}O_2$ (156.2): calcd. C 69.19, H 10.32; found C 69.15, H 10.67.

(E)-1-(Hex-2-enyloxy)-butan-2-one (**2c**): 85% Yield from amide **1c** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:10). - R_f = 0.18 (diethyl ether/ light petroleum, 1:10). - IR (film): ν = 1719 (s, C=O), 1671 (w, C=C), 1108 (s, COC) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.90 (t, *J* = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.07 (t, *J* =7.4 Hz, 3H, $COCH_2CH_3$). 1.41 (m, 2H, $CHCH_2CH_2$), 2.03 (m, 2H, $CHCH_2CH_2$), 3.99 (dd, *J* = 6.4 Hz/ 1.0 Hz, 2H, $CHCH_2O$), 4.03 (s, 2H, OCH_2CO), 5.55 (dtt, *J* = 15.4 Hz/ 6.0 Hz/ 1.2 Hz, 1H, $CHCH_2O$), 5.72 (dtt, *J* = 15.4 Hz/ 6.7 Hz/ 1.0 Hz, 1H, $CHCH_2CH_3$) ppm. - ^{13}C NMR (75 MHz): δ = 7.26, 13.68, 22.20, 32.23, 34.37, 72.18, 74.45, 125.63, 135.75, 209.65 ppm. - GC/MS (70 eV): *m/z* (%) = 99 [60, (*n*-Pr)$HCCHCH_2O^+$], 57 (100, $C_2H_5CO^+$). - $C_{10}H_{18}O_2$ (170.3): calcd. C 70.55, H 10.66; found C 70.35, H 10.78.

(E)-2-(But-2-enyloxy)-1-phenyl-ethan-1-one[27] (**2d**): 85% Yield from amide **1a** after distillation (b.p. 70 - 74 °C/ 0.1 mbar). - R_f = 0.55 (diethyl ether/ light petroleum, 1:2). - ^1H NMR (300 MHz): δ = 1.71 (ddt, *J* = 6.4 Hz/ 1.4 Hz/ 1.1 Hz, 3H, $CHCH_3$), 4.06 (m, 2H, $CHCH_2O$), 4.22 (s, 2H, OCH_2CO), 5.62 (m, 1H, $CHCH_2O$), 5.76 (dqt, *J* = 15.4 Hz/ 6.1 Hz/ 1.1 Hz, 1H, $CHCH_3$), 7.45 (m, 2H, CH_{meta}), 7.57 (m, 1H, CH_{para}), 7.92 (m, 2H, CH_{ortho}) ppm. - ^{13}C NMR (75 MHz): δ = 17.76, 72.11, 72.28, 126.84, 127.85, 128.66, 130.82, 133.45, 134.98, 196.44 ppm.

(E)-2-(Hex-2-enyloxy)-1-phenyl-ethan-1-one (**2e**): 76% Yield from amide **1c** after column chromatography (silica gel, diethyl ether/ light petroleum, 1:10). - R_f = 0.26 (diethyl ether/ light petroleum, 1:10). - IR (film): ν = 1703 (s, CO), 1136 (s, COC) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.90 (t, *J* = 7.3 Hz, 3H, $CH_2CH_2CH_3$), 1.40 (m, 2H, $CHCH_2CH_2$), 2.03 (m, 2H, $CHCH_2CH_2$), 4.10 (m, 2H, $CHCH_2O$), 4.72 (s, 2H, OCH_2CO), 5.60 (dtt, *J* = 15.4 Hz/ 6.4 Hz/ 1.2 Hz, 1H, $CHCH_2O$), 5.74 (dtt, *J* = 15.4 Hz/ 6.4 Hz/ 1.0 Hz, 1H, $CHCH_2CH_3$), 7.45 (m, 2H, CH_{meta}), 7.57 (m, 1H, CH_{para}), 7.92 (m, 2H, CH_{ortho}) ppm. - ^{13}C NMR (75 MHz): δ = 13.68, 22.14, 34.34, 72.23, 72.28, 125.64, 127.89, 128.67, 133.45, 135.04, 135.98, 196.48 ppm. - GC/MS (70 eV): *m/z* (%) = 105 (100, $C_6H_5CO^+$), 77 (31, $C_6H_5^+$). - $C_{14}H_{18}O_2$ (218.2): calcd. C 77.06, H 8.31; found C 77.62, H 8.30.

(S)-1-[1-((E)-(But-2-enyloxymethyl)-1-propylidenamino]-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S*)-**3a**]: 86% Yield from ketone **2a** after distillation (b.p. 85 - 90 °C/ 0.05 mbar). - $[\alpha]_D^{RT}$: +448.5 (*c* = 1.0, $CHCl_3$). - R_f = 0.50, 0.43 (diethyl ether/ light petroleum, 1:2). - $(E)_{CN}/(Z)_{CN}$ = 44/ 56, Determined by ^{13}C NMR. - IR (film): ν = 1670 (w, C=C), 1630 (w, C=N), 1100 (s, COC) cm^{-1}. - ^1H NMR (300 MHz), Data of the isomeric mixture $(E)_{CN}/(Z)_{CN}$: δ = 0.85 [m, 6H, $C(CH_2CH_3)_2$], 1.14/ 1.10 (t, *J* = 7.4 Hz, 3H, $CNCH_2CH_3$), 1.30-2.00 [m, 8H, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 1.72 (m, 3H, $CHCH_3$), 2.20-2,60 (m, 3H, $CNCH_2CH_3$, *H*CHN), 2.99, 3.25 (dt, *J* = 9.9 Hz/ 6.3 Hz, 1H, HC*H*N), 3.32/ 3.31 (s, 3H, OCH_3), 3.57 (m, 1H, CHN), 3.87 (m, 2H, $CHCH_2O$), 3.94, 4.48 (d, *J* =14.3 Hz, 2H (*Z*), O*H*CHCN), 3.97, 4.05 (d, *J* = 12.5 Hz, 2H (*E*), O*H*CHCN), 5.60 (m, 1H, $CHCH_2O$), 5.71 (m, 1H, $CHCH_3$) ppm. - ^{13}C NMR (75 MHz), Data of the isomeric mixture $(E)_{CN}/(Z)_{CN}$: δ = 8.04, 8.07, 8.16, 8.20, 10.38/ 11.84, 17.80/ 17.78), 22.86/ 26.45, 23.45, 24.71, 24.79, 25.21, 25.33, 27.05, 27.11, 50.47/ 50.44, 57.88/ 57.63, 70.82/ 66.75, 71.77, 72.51/ 72.63, 80.14/ 80.09, 127.46/ 127.28, 129.73/ 129.67, 163.48/ 165.88 ppm. - GC/MS (70 eV): *m/z* (%) = 209 (61, $M^+-H_3COC(C_2H_5)_2$), 70 (33, $C_4H_8N^+$), 55 (100, $CH_3HCCHCH_2^+$). - $C_{18}H_{34}N_2O_2$ (310.5): calcd. C 69.63, H 11.04, N 9.02; found C 69.66, H 11.42, N 9.36.

(S)-2-(1-Ethyl-1-methoxypropyl)-1-[1-(3-methyl-but-2-enyloxymethyl)-1-propylidenamino]-pyrrolidine [(*S*)-**3b**]: 95% Yield from ketone **2b** after distillation (b.p. 96 - 105 °C/ 0.05 mbar). - $[\alpha]_D^{RT}$: +435.0 (*c* = 1.0, $CHCl_3$). - R_f = 0.47, 0.42 (diethyl ether/ light petroleum, 1:2). - $(E)_{CN}/(Z)_{CN}$ = 1/ 1, Determined by ^{13}C NMR. - IR (film): ν = 1675 (w, C=C), 1630 (w, C=N), 1080 (s, COC) cm^{-1}. - ^1H NMR (300 MHz), Data of the isomeric mixture $(E)_{CN}/(Z)_{CN}$: δ = 0.83, 0.86 [t, *J* = 6.4 Hz, 6H, $C(CH_2CH_3)_2$], 1.14/ 1.10 (t, *J* = 7.7 Hz, 3H, $CNCH_2CH_3$), 1.30-2.00 [m, 8H, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 1.68 [s, 3H, $C(CH_3)_{cis}$], 1.75 [s, 3H, $C(CH_3)_{trans}$], 2.20-2,60 (m, 3H, $CNCH_2CH_3$, *H*CHN), 3.01, 3.26 (dt, *J* = 9.7 Hz/ 6.4 Hz, 1H, HC*H*N), 3.32 (s, 3H, OCH_3), 3.56 (m, 1H, CHN), 3.94 (m, 2H, $CCHCH_2O$), 3.96, 4.50 (d, *J* =14.1 Hz, 2H (*Z*), O*H*C*H*CN), 3.99, 4.05 (d, *J* = 12.1 Hz, 2H (*E*), O*H*C*H*CN), 5.36 (m, 1H, $CCHCH_2O$) ppm. - ^{13}C NMR (75 MHz), Data of the isomeric mixture $(E)_{CN}$, $(Z)_{CN}$: δ = 8.03, 8.07, 8.15, 8.22, 10.39, 11.84, 18.00, 18.04, 22.83, 23.47, 24.70, 24.80, 26.41, 27.04, 27.11, 25.78, 25.81, 50.43, 50.46, 57.70, 57.92, 66.56, 66.86, 67.66, 71.97, 72.54, 72.60, 80.11, 80.17, 120.86, 121.04, 137.21, 137.33, 163.62, 165.97 ppm. - GC/MS (70 eV): *m/z* (%) = 324 (0.8, M^+), 223 [48, $M^+{-}H_3COC(C_2H_5)_2$], 70 (39, $C_4H_8N^+$), 69 (100, $(CH_3)_2CCHCH_2^+$). - $C_{19}H_{36}N_2O_2$ (324.4): calcd. C 70.32, H 11.18, N 8.63; found C 70.36, H 11.38, N 9.08.

(S)-2-(1-Ethyl-1-methoxypropyl)-1-[1-((E)-Hex-2-enyloxymethyl)-1-propylidenamino]-pyrrolidine [(*S*)-**3c**]: 95% Yield from ketone **2c** after distillation (b.p. 96 - 105 °C/ 0.02 mbar). - $[\alpha]_D^{RT}$: +406.5 (*c* = 1.4, $CHCl_3$). - R_f = 0.55, 0.47 (diethyl ether/ light petroleum, 1:2). - $(E)_{CN}/(Z)_{CN}$ = 1/ 1, Determined by ^{13}C NMR. - IR (film): ν = 1670 (w, C=C), 1630 (w, C=N), 1085 (s, COC) cm^{-1}. - ^1H NMR (300 MHz), Data of the isomeric mixture $(E)_{CN}/(Z)_{CN}$: δ = 0.83, 0.86 [t, *J* = 7.4 Hz, 6H, $C(CH_2CH_3)_2$], 0.91 (t, *J* = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 1.14/ 1.10 (t, *J* = 7.7 Hz, 3H, $CNCH_2CH_3$), 1.30-2.10 [m, 12H, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$, 4 $CH_2CH_2CH_3$], 2.20-2.60 (m, 3H, $CNCH_2CH_3$, *H*CHN), 3.00, 3.25 (dt, *J* = 10.1 Hz/ 6.1 Hz, 1H , HC*H*N), 3.31, 3.32 (s, 3H, OCH_3), 3.56 (dt, *J* = 14.1 Hz/ 8.1 Hz, 1H, CHN), 3.90 (m, 2H, $CHCH_2O$), 3.95, 4.50 (d, *J* =14.1 Hz, 2H (Z), O*H*C*H*CN), 3.98, 4.05 (d, *J* = 11.8 Hz, 2H (*E*), O*H*C*H*CN), 5.57 (m, 1H, $CHCH_2O$), 5.70 (m, 1H, $CHCH_2CH_2$) ppm. - ^{13}C NMR (75 MHz, $CDCl_3$), Data of the isomeric mixture $(E)_{CN}/(Z)_{CN}$: δ = 8.04, 8.07, 8.14, 8.20, 10.38/ 11.84, 13.68, 13.70, 22.28, 22.86/ 26.49, 23.45, 23.47 24.69, 24.79, 25.21, 25.32, 27.04, 27.11, 38.38, 34.41, 50.45, 50.47, 57.62, 57.89, 70.89/ 66.73, 71.71, 71.89, 72.51, 72.63, 80.10, 80.16, 126.05, 126.23, 134.87, 134.90, 163.47/ 165.93 ppm. - GC/MS (70 eV): *m/z* (%) = 338 (1.3, M^+), 237 [100, $M^+{-}H_3COC(C_2H_5)_2$], 83 [75, C(*n*-Pr)$HCCHCH_2^+$], 70 (48, $C_4H_8N^+$). - $C_{20}H_{38}N_2O_2$ (338.5): calcd. C 70.96, H 11.31, N 8.28; found C 70.97, H 11.70, N 8.72.

(S)-1-[2-((E)-(But-2-enyloxy)-1-phenyl-1-ethylidenamino]-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S*)-**3d**]: 95% Yield from ketone **2d** column chromatography (silica gel, diethyl ether/ light petroleum, 1:7, 2.5% NEt_3). - $[\alpha]_D^{RT}$: +805.5 (*c* = 1.0, $CHCl_3$). - R_f = 0.35, 0.30 (diethyl ether/ light petroleum, 1:4). - $(E)_{CN}/(Z)_{CN}$ = 44/ 56, Determined by ^{13}C NMR. - IR (film): ν = 1670 (w, C=C), 1590 (w, C=N), 1085 (s, COC) cm^{-1}. - ^1H NMR (300 MHz), Data of the isomeric mixture $(E)_{CN}/(Z)_{CN}$: δ = 0.93 [m, 6H, $C(CH_2CH_3)_2$], 1.40-2.05 [m, 8H, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 1.69 (m, 3H, $CHCH_3$), 2.38, 2.81, 3.35 (m, 2H, *H*C*H*N), 3.31/ 3.36 (s, 3H, OCH_3), 3.75-3.94 (m, 3H, $CHCH_2O$, CHN), 4.18, 4.40 (d, *J* =11.8 Hz, 2H (*E*), O*H*C*H*CN), 4.44, 4.56 (d, *J* = 12.4 Hz, 2H (*Z*), O*H*C*H*CN), 5.52 (m, 1H, $CHCH_2O$), 5.63 (m, 1H, $CHCH_3$), 7.20-7.37 (m, 3H, CH_{meta}, CH_{para}), 7.47/ 7.72 (m, 2H, CH_{ortho}) ppm. - ^{13}C NMR (75 MHz), Data of the isomeric mixture $(E)_{CN}/(Z)_{CN}$: δ = 8.05, 8.27, 17.76/ 17.73, 23.52/ 23.44, 24.37, 25.09, 25.22, 27.09/

27.14, 50.41/ 50.47, 57.64/ 59.54, 70.10/ 65.53, 74.60/ 71.41, 72.85/ 73.09, 80.31/ 79.96, 126.68, 127.13, 127.63, 128.06, 128.09, 128.15, 127.13, 127.54, 129.44/ 129.99, 137.45, 137.63, 145.57, 154.19 ppm. - MS (70 eV): *m/z* (%) = 358 (2.8, M^+), 257 [100, M^+–$H_3COC(C_2H_5)_2$], 70 (22, $C_4H_8N^+$), 55 (77, $CH_3HCCHCH_2^+$). - HRMS: calcd. for $C_{22}H_{34}N_2O_2$ 358.2620; found 358.2619.

(S)-2-(1-Ethyl-1-methoxypropyl)-1-[2-((E)-hex-2-enyloxy)-1-phenyl-1-ethylidenamino]-pyrrolidine [(*S*)-**3e**]: 86% Yield from ketone **2e** after column chromatography (diethyl ether/ light petroleum, 1:4, 2.5% NEt_3). - $[\alpha]_D^{RT}$: +778.8 (*c* = 1.0, $CHCl_3$). - R_f = 0.21 (diethyl ether/ light petroleum, 1:4, 2.5%NEt_3). - $(E)_{CN}$/ $(Z)_{CN}$ = 42/ 58, Determined by ^{13}C NMR. - IR (film): ν = 1670 (w, C=C), 1585 (w, C=N), 1085 (s, COC) cm^{-1}. - ^1H NMR (300 MHz), Data of the isomeric mixture $(E)_{CN}$/ $(Z)_{CN}$: δ = 0.84-0.98 [m, 9H, 3 $CH_2CH_2CH_3$, 6 $C(CH_2CH_3)_2$], 1.30-1.90 [m, 10H, 4 ring-CH_2, 2 $CH_2CH_2CH_3$, 4 $C(CH_2CH_3)_2$], 1.98 (m, 2H, $CH_2CH_2CH_3$), 2.38, 2.81, 3.35 (m, 2H, *H*CHN), 3.31/ 3.36 (s, 3H, OCH_3), 3.75-3.95 (m, 3H, $CHCH_2O$, CHN), 4.19, 4.57 (d, *J* =11.8 Hz, 2H (*E*), O*H*CHCN), 4.44, 4.57 (d, *J* = 12.4 Hz, 2H (*Z*), O*H*CHCN), 5.49 (m, 1H, $CHCH_2O$), 5.62 (m, 1H, $CHCCH_2CH_2$), 7.20-7.37 (m, 3H, CH_{meta}, CH_{para}), 7.47/ 7.73 (m, 2H, CH_{ortho}) ppm. - ^{13}C NMR (75 MHz), Data of the isomeric mixture $(E)_{CN}$/ $(Z)_{CN}$: δ = 8.05, 8.27, 13.67, 22.23/ 22.18, 23.52/ 23.46, 24.37, 25.11, 25.23, 27.09/ 27.15, 34.39/ 34.34, 50.42/ 50.50, 57.65/ 59.55, 70.13/ 65.50, 74.47/ 71.54, 72.87/ 73.10, 80.34/ 79.98, 126.40, 125.88, 126.67, 127.55, 127.65, 128.07, 128.10, 128.15, 134.66/ 135.24, 137.64/ 137.50, 145.61, 154.04 ppm. - MS (70 eV): *m/z* (%) = 105 (100), 83 [(*n*-Pr)$HCCHCH_2^+$), 77 (24, $C_6H_5^+$). - $C_{24}H_{38}N_2O_2$ (386.6): calcd. C 74.57, H 9.91, N 7.25; found C 74.57, H 10.09, N 7.57.

(2S,2'R,3'S)-1-(1'-Ethyl-2'-hydroxy-3'-methyl-1'-pent-4'-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R,S*)-**4a**]: 94% Yield from hydrazone (*S*)-**3a** after column chromatography (diethyl ether/ light petroleum, 1:3, 2% NEt_3). - $[\alpha]_D^{RT}$: +339.9 [$(E)_{CN}$ isomer, *c* = 1.1, $CHCl_3$], after separation by HPLC (diethylether/ light petroleum, 3:7, flow: 18 ml/ min, $R_t(E)_{CN}$ = 11.4 min, $R_t(Z)_{CN}$ = 15.7 min). - R_f = 0.38 [$(E)_{CN}$], 0.30 [$(Z)_{CN}$] (diethyl ether/ light petroleum, 1:1). - $(E)_{CN}$/ $(Z)_{CN}$ = 1/ 1. - IR (film): ν = 3400 (br, OH), 1710 (w, C=N), 1640 (m, C=C) cm^{-1}. - ^1H NMR (300 MHz): $(E)_{CN}$ isomer: δ = 0.83, 0.85 [t, *J* = 7.4 Hz, 6H, $C(CH_2CH_3)_2$], 0.86 (d, *J* = 7.1 Hz, 3H, $CHCH_3$), 1.10 (t, *J* = 7.7 Hz, 3H, $CNCH_2CH_3$), 1.30-2.05 [m, 9H, CN*H*$CHCH_3$, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.35-2.50 (m, 2H, *H*CHN, $CHCH_3$), 2.85 (m, 1H, $CNHCHCH_3$), 3.26 (dt, *J* = 9.7 Hz/ 6.1 Hz, 1H, HC*H*N), 3.31 (s, 3H, OCH_3), 3.61 (t, *J* = 8.1 Hz, 1H, CHN), 4.33 (m, 1H, C*H*OH), 4.44 (s, 1H, OH), 5.08 (m, 2H, HC=CH_2), 6.01 (ddd, *J* = 17.5 Hz/ 10.4 Hz/ 7.4 Hz, 1H, *H*C=CH_2) ppm ;$(Z)_{CN}$ isomer: δ = 0.88, 0.90 [t, *J* = 7.4 Hz, 6H, $C(CH_2CH_3)_2$], 1.12 (d, *J* = 7.1 Hz, 3H, $CHCH_3$), 1.12 (t, *J* = 7.4 Hz, 3H, $CNCH_2CH_3$), 1.30-2.05 [m, 8H, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.25 (m, 1H, CN*H*$CHCH_3$), 2.35 (m, 1H, $CNHCHCH_3$), 2.45-2.65 (m, 2H, *H*CHN, $CHCH_3$), 2.94 (m, 1H, HC*H*N), 3.17 (s, 3H, OCH_3), 3.37 (dd, *J* = 10.1 Hz/ 5.4 Hz, 1H, CHN), 4.84 (d, *J* = 7.4 Hz, 1H, C*H*OH), 5.06 (m, 2H, HC=CH_2), 5.76 (ddd, *J* = 17.8 Hz/ 10.4 Hz/ 7.4 Hz, 1H, *H*C=CH_2), 6.39 (s, 1H, OH) ppm. - ^{13}C NMR (75 MHz): $(E)_{CN}$ isomer: δ = 8.01, 8.20, 10.13, 12.07, 23.09, 23.50, 24.06, 25.08, 27.04, 41.24), 50.40, 57.42, 72.62, 73.05, 79.97, 113.98, 142.01, 162.60 ppm; $(Z)_{CN}$ isomer: δ = 8.27, 8.33, 11.25, 15.46, 23.65, 25.14, 25.68, 26.14, 26.66, 40.05, 49.61, 57.31, 69.59, 73.90, 80.90, 114.78, 140.86, 173.28 ppm. - MS (70 eV): *m/z* (%) = 310 (0.7, M^+), 209 (100, M^+–$H_3COC(C_2H_5)_2$), 70 (29, $C_4H_8N^+$). - $C_{18}H_{34}N_2O_2$ (310.5): calcd. C 69.63, H 11.04, N 9.02; found C 69.22, H 11.05, N 9.24.

(2S,2'R)-1-(3',3'-Dimethyl-1'-ethyl-2'-hydroxy-1'-pent-4'-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R*)-**4b**]: 92% Yield from hydrazone (*S*)-**3b** after column chromatography (diethyl ether/ light petroleum, 1:4, 2% NEt_3). - $[\alpha]_D^{RT}$: +263.2 [$(E)_{CN}$ isomer, c = 1.1, $CHCl_3$], after separation by HPLC (diethylether/ light petroleum, 3:7, flow: 18 ml/ min, $R_t(E)_{CN}$ = 9.0 min, $R_t(Z)_{CN}$ = 12.4 min). - R_f = 0.53 [$(E)_{CN}$], 0.41 [$(Z)_{CN}$] (diethyl ether/ light petroleum, 1:2). - $(E)_{CN}$/ $(Z)_{CN}$ = 6/ 4. - IR (film): ν = 3400 (br, OH), 1640 (m, C=C) cm^{-1}. - ^1H NMR: $(E)_{CN}$ isomer (500 MHz): δ = 0.82, 0.85 [t, J = 7.4 Hz, 6H, $C(CH_2CH_3)_2$], 0.94, 1.10 [s, 6H, $C(CH_3)_2$], 1.05 (t, J = 7.6 Hz, 3H, $CNCH_2CH_3$), 1.30-1.70 [m, 4H, $C(CH_2CH_3)_2$], 1.70-2.05 (m, 5H, ring-CH_2, CN*H*$CHCH_3$), 2.44 (ddd, J = 9.9 Hz/ 7.5 Hz/ 6.7 Hz, 1H, *H*CHN), 2.80 (m, 1H, CNHC*H*CH_3), 3.28 (dt, J = 9.9 Hz/ 6.4 Hz, 1H, HC*H*N), 3.30 (s, 3H, OCH_3), 3.61 (t, J = 8.2 Hz, 1H, CHN), 4.04 (d, J = 6.6 Hz, 1H, C*H*OH), 4.50 (d, J = 6.7 Hz, 1H, OH), 4.98 (m, 2H, HC=CH_2), 5.93 (m, 1H, *H*C=CH_2) ppm; $(Z)_{CN}$ Isomer (300 MHz): δ = 0.89, 0.93 [t, J = 7.7 Hz, 6H, $C(CH_2CH_3)_2$], 1.04, 1.15 [s, 6H, $C(CH_3)_2$], 1.09 (t, J = 7.4 Hz, 3H, $CNCH_2CH_3$), 1.45-2.05 [m, 8H, 4 $C(CH_2CH_3)_2$, 4 ring-CH_2], 2.22 (m, 1H, CN*H*$CHCH_3$), 2.41 (m, 1H, CNHC*H*CH_3), 2.61 (m, 1H, *H*CHN), 2.87 (m, 1H, HC*H*N), 3.11 (s, 3H, OCH_3), 3.31 (m, 1H, CHN), 4.32 (s, 1H, OH), 5.04 (m, 2H, HC=CH_2), 5.32 (s, 1H, OH), 6.16 (dd, J = 17.6 Hz/ 11.0 Hz, 1H, *H*C=CH_2) ppm. - ^{13}C NMR: $(E)_{CN}$ isomer (125 MHz): δ = 8.03, 8.18, 10.07, 20.06, 25.03), 23.38, 27.02, 24.62, 25.12, 25.61, 42.52, 50.45, 58.01, 72.88, 76.20, 79.94, 111.91), 145.55, 162.12 ppm; $(Z)_{CN}$ Isomer (75 MHz): δ = 8.28, 8.42, 11.16, 23.67, 26.20, 23.75, 25.46, 25.91, 26.31, 26.66, 39.44, 49.17, 57.14, 68.05, 74.25, 81.40, 111.49, 144.93, 175.65 ppm. - MS (70 eV): *m/z* (%) = 324 (0.7, M^+), 223 [100, M^+–$H_3COC(C_2H_5)_2$], 70 (26, $C_4H_8N^+$). - HRMS calcd. for [M^+–C_2H_5] $C_{17}H_{31}N_2O_2$ 295.2386; found 295.2387.

(2S,2'R,3'S)-1-(1'-Ethyl-2'-hydroxy-3'-propyl-1'-pent-4'-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R,S*)-**4c**]: 89% Yield from hydrazone (*S*)-**3c** after column chromatography (diethyl ether/ light petroleum, 1:4, 2% NEt_3). - $[\alpha]_D^{RT}$: +251.8 [$(E)_{CN}$ isomer, c = 1.0, $CHCl_3$], after separation by HPLC (diethyl ether/ light petroleum, 1:3, flow: 18 ml/ min, $R_t(E)_{CN}$ = 9.5 min. - R_f = 0.56 (diethyl ether/ light petroleum, 1:2). - $(E)_{CN}$ > 90%. - IR (film): ν = 3400 (br, OH), 1640 (m, C=C) cm^{-1}. - ^1H NMR (300 MHz), $(E)_{CN}$ isomer: δ = 0.80-0.90 [m, 9H, 3 $CH_2CH_2CH_3$, 6 $C(CH_2CH_3)_2$], 1.09 (t, J = 7.4 Hz, 3H, $CNCH_2CH_3$), 1.10-2.05 [m, 13H, CN*H*$CHCH_3$, 4 $CH_2CH_2CH_3$, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.13 (m, 1H, C*H*HC=CH_2), 2.44 (dt, J = 9.7 Hz/ 7.4 Hz, 1H, *H*CHN), 2.82 (m, 1H, CNHC*H*CH_3), 3.26 (dt, J = 9.7 Hz/ 6.0 Hz, 1H, HC*H*N), 3.31 (s, 3H, OCH_3), 3.61 (t, J = 8.1 Hz, 1H, CHN), 4.28 (dd, J = 4.7 Hz/ 3.0 Hz, 1H, C*H*OH), 4.42 (d, J = 5.3 Hz, 1H, OH), 5.08 (m, 2H, HC=CH_2), 5.88 (m, 1H, *H*C=CH_2) ppm. - ^{13}C NMR (75 MHz): δ = 8.02, 8.19, 10.14, 14.12, 20.35, 23.32, 23.47, 24.41, 25.07, 27.04, 29.17, 48.12, 50.41, 57.38, 72.60, 73.76, 79.67, 115.41, 140.75, 162.81 ppm. - MS (70 eV): *m/z* (%) = 338 (0.2, M^+), 237 [100, M^+–$H_3COC(C_2H_5)_2$]. - HRMS calcd. for [M^+–C_2H_5] $C_{18}H_{33}N_2O_2$ 309.2542; found 309.2542.

(2S,2'R,3'S)-2-(1-Ethyl-1-methoxypropyl)-1-(2'-hydroxy-3'-methyl-2'-phenyl-1'-pent-4'-enylidenamino)-pyrrolidine [(*S,R,S*)-**4d**]: 98% Yield from hydrazone (*S*)-**3d** after column chromatography (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{RT}$: +409.5 [$(E)_{CN}$ isomer, c = 1.0, CH_2Cl_2]; +300.9 [$(Z)_{CN}$ isomer, c = 1.0, CH_2Cl_2] after separation by HPLC (diethyl ether/ light petroleum, 3:7, flow: 18 ml/ min, $R_t(E)_{CN}$ = 18.1 min, $R_t(Z)_{CN}$ = 11.0 min). - R_f = 0.36 [$(E)_{CN}$], 0.44 [$(Z)_{CN}$] (diethyl ether/ light petroleum, 1:2). - $(E)_{CN}$/ $(Z)_{CN}$ = 4/ 6. - IR (film): ν = 3400 (br, OH), 1640 (w, C=C) cm^{-1}. - ^1H NMR (500 MHz): $(E)_{CN}$ isomer: δ =

0.85 [t, J = 7.5 Hz, 6H, $C(CH_2CH_3)_2$], 1.06 (d, J = 6.9 Hz, 3H, $CHCH_3$), 1.40-1.90 [m, 8H, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.48 (dt, J = 10.2 Hz/ 7.7 Hz, 1H, *H*CHN), 2.56 (m, 1H, $CHCH_3$), 2.68 (ddd, J = 9.9 Hz/ 6.9 Hz/ 5.3 Hz, 1H, HC*H*N), 3.21 (s, 3H, OCH_3), 3.68 (dd, J = 8.4 Hz/ 6.6 Hz, 1H, CHN), 4.04 (d, J = 4.6 Hz, 1H, OH), 4.30 (t, J = 3.6 Hz, 1H, C*H*OH), 5.01 (ddd, J = 17.2 Hz/ 1.7 Hz/ 1.4 Hz, 1H, HC=CHH_{cis}), 5.03 (ddd, J = 10.5 Hz/ 1.7 Hz/ 1.1 Hz, 1H, HC=CHH_{trans}), 5.93 (ddd, J = 17.3 Hz/ 10.5 Hz/ 7.0 Hz, 1H, *H*C=CH_2), 7.26 (m, 2H, CH_{ortho}), 7.29-7.38 (m, 3H, CH_{para}, CH_{meta}) ppm; $(Z)_{CN}$ isomer: δ = 0.92, 0.97 [t, J = 7.5 Hz, 6H, $C(CH_2CH_3)_2$], 1.08 (d, J = 6.6 Hz, 3H, $CHCH_3$), 1.50-2.10 [m, 8H, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.42 (m, 1H, $CHCH_3$), 2.74 (td, J = 9.5 Hz/ 6.7 Hz, 1H, *H*CHN), 3.05 (m, 1H, HC*H*N), 3.12 (s, 3H, OCH_3), 3.50 (dd, J = 10.5 Hz/ 5.7 Hz, 1H, CHN), 4.73 (ddd, J = 17.3 Hz/ 1.8 Hz/ 1.3 Hz, 1H, HC=CHH_{cis}), 4.88 (ddd, J = 10.5 Hz/ 1.8 Hz/ 0.9 Hz, 1H, HC=CHH_{trans}), 5.28 (d, J = 7.9 Hz, 1H, C*H*OH), 5.59 (ddd, J = 17.3 Hz/ 10.5 Hz/ 7.4 Hz, 1H, *H*C=CH_2), 6.65 (s, 1H, OH), 7.32-7.37 (m, 3H, CH_{meta}, CH_{para}), 7.61 (m, 2H, CH_{ortho}) ppm. - ^{13}C NMR (125 MHz): $(E)_{CN}$ isomer: δ = 7.74, 8.30, 12.79, 23.43, 24.32, 24.86, 26.87, 40.13, 50.38, 57.71, 72.53, 77.73, 80.14, 114.25, 128.06, 128.34, 128.14, 137.32, 141.76, 151.27 ppm; $(Z)_{CN}$ isomer: δ = 8.28, 8.46, 15.12, 23.82, 25.39, 26.40, 26.65, 40.44, 49.43, 57.62, 69.38, 74.05, 81.31, 115.01, 127.72, 128.06, 128.82, 137.82, 140.07, 172.54 ppm. - MS (70 eV) : *m/z* (%) = 358 (1.1, M^+), 257 [100, M^+–$H_3COC(C_2H_5)_2$], 70 (34, $C_4H_8N^+$). - HRMS: calcd. for $C_{22}H_{34}N_2O_2$ 358.2620; found 358.2624.

(2S,2´R,3´S)-2-(1-Ethyl-1-methoxypropyl)-1-(2´-hydroxy-2´-phenyl-3´-propyl-1´-pent-4´-enyliden-amino)-pyrrolidine [(*S,R,S*)-**4e**]: 100% Yield from hydrazone (*S*)-**3e** after column chromatography (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{RT}$: +402.2 [$(E)_{CN}$ isomer, c = 1.1, CH_2Cl_2]; +320.4 [$(Z)_{CN}$ isomer, c = 1.1, CH_2Cl_2] after separation by HPLC (diethyl ether/ light petroleum, 3:7, flow: 18 ml/ min, $R_t(E)_{CN}$ = 14.3 min, $R_t(Z)_{CN}$ = 9.9 min). - R_f = 0.15 [$(E)_{CN}$], 0.51 [$(Z)_{CN}$] (diethyl ether/ light petroleum, 1:2). - $(E)_{CN}$/ $(Z)_{CN}$ = 4/ 6. - IR (film): ν = 3400 (br, OH), 1640 (w, C=C) cm^{-1}. - ^1H NMR (300 MHz): $(E)_{CN}$ isomer: δ = 0.85-0.92 [m, 9H, 6 $C(CH_2CH_3)_2$, 3 $CH_2CH_2CH_3$], 1.10-1.90 [m, 12H, 4 ring-CH_2, 4 $CH_2CH_2CH_3$, 4 $C(CH_2CH_3)_2$], 2.29 (m, 1H, C*H*HC=CH_2), 2.47 (dt, J = 10.2 Hz/ 7.7 Hz, 1H, *H*CHN), 2.67 (ddd, J = 10.2 Hz/ 6.6 Hz/ 5.5 Hz, 1H, HC*H*N), 3.21 (s, 3H, OCH_3), 3.69 (t, J = 7.4 Hz, 1H, CHN), 3.84 (s, 1H, OH), 4.28 (d, J = 4.4 Hz, 1H, C*H*OH), 4.91 (ddd, J = 17.0 Hz/ 1.9 Hz/ 0.8 Hz, 1H, HC=CHH_{cis}), 5.03 (dd, J = 10.4 Hz/ 1.9Hz, 1H, HC=CHH_{trans}), 5.76 (ddd, J = 17.0 Hz/ 10.2 Hz/ 8.8 Hz, 1H, *H*C=CH_2), 7.24-7.40 (kompl. Ber, 5H, CH_{arom}) ppm; $(Z)_{CN}$ isomer: δ = 0.79 (t, J = 7.1 Hz, 3H, $CH_2CH_2CH_3$), 0.91, 0.98 [t, J= 7.7 Hz, 6H, $C(CH_2CH_3)_2$], 0.80-2.10 [m, 12H, 4 ring-CH_2, 4 $CH_2CH_2CH_3$, 4 $C(CH_2CH_3)_2$], 2.24 (m, 1H, C*H*HC=CH_2), 2.74 (td, J = 9.1 Hz/ 6.9 Hz, 1H, *H*CHN), 3.02 (m, 1H, HC*H*N), 3.10 (s, 3H, OCH_3), 3.49 (dd, J = 10.4 Hz/ 5.5 Hz, 1H, CHN), 4.56 (ddd, J = 17.3 Hz/ 1.9 Hz/ 0.6 Hz, 1H, HC=CHH_{cis}), 4.88 (dd, J = 10.2 Hz/ 1.9Hz, 1H, HC=CHH_{trans}), 5.38 (d, J = 8.9 Hz, 1H, C*H*OH), 5.42 (ddd, J = 17.3 Hz/ 10.2 Hz/ 9.1 Hz, 1H, *H*C=CH_2), 6.44 (s, 1H, OH), 7.29-7.37 (m, 3H, CH_{para}, CH_{meta}), 7.62 (m, 2H, CH_{ortho}) ppm. - ^{13}C NMR (75 MHz): $(E)_{CN}$ isomer: δ = 7.95, 8.29, 14.25, 20.30, 23.41, 24.43, 24.88, 26.90, 30.01, 46.96, 50.37, 57.67, 72.55, 78.45, 80.15, 115.88, 128.00, 128.13, 128.18, 137.30, 140.15, 151.52 ppm; $(Z)_{CN}$ isomer: δ = 8.28, 8.46, 14.09, 19.94, 23.87, 25.52, 26.49, 26.61, 31.93, 46.51, 49.35, 57.56, 69.17, 73.00, 81.43, 116.71, 128.67, 127.84, 127.87), 137.80, 138.37, 172.85 ppm. - MS (70 eV): *m/z* (%) = 386 (0.8, M^+), 285 [100, M^+–$H_3COC(C_2H_5)_2$], 70 (33, $C_4H_8N^+$). - HRMS: calcd. for $C_{22}H_{32}N_2O_2$ 357.2542; found 357.2545.

(4R,5S)-4-Hydroxy-5-methyl-hept-6-en-3-one [(*R*,*S*)-**5a**]: 81% Yield from hydrazone **4a** after column chromatography (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{RT}$: –148.4 (*c* = 1.0, $CHCl_3$), After HPLC of **4a**. - R_f = 0.36 (diethyl ether/ light petroleum, 1:2). - *syn* = 97% (> 99% After HPLC of **4a**), determined by GC (SE-30, 80-1-95-10-300): R_t = 7.7 min, - *ee* = 81% (96% After HPLC of **4a**), determined by ^1H NMR spectroscopy with (–)-1-(9-anthryl)-2,2,2-trifluoroethanol as cosolvent (4 equiv.). - IR (film): ν = 3500 (br, OH), 1710 (s, C=O), 1640 (m, C=C) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.89 (d, *J* = 7.1 Hz, 3H, $CHCH_3$), 1.13 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 2.50, 2.52 (dq, *J* = 17.8 Hz/ 7.4 Hz, 2H, *H*CHCH$_3$), 2.67 (m, 1H, C*H*CH$_3$), 3.41 (d, *J* = 5.0 Hz, 1H, OH), 4.21 (dd, *J* = 5.0 Hz/ 3.0 Hz, 1H, C*H*OH), 5.11 (ddd, *J* = 10.1 Hz/ 1.7 Hz/ 1.3 Hz, 1H, HC=CHH_{trans}), 5.14 (ddd, *J* = 17.5 Hz/ 1.7 Hz/ 1.3 Hz, 1H, HC=CHH_{cis}), 5.95 (ddd, *J* = 17.1 Hz/ 10.4 Hz/ 7.1 Hz, 1H, C*H*=CH$_2$) ppm. - ^{13}C NMR (75 MHz): δ = 7.54, 12.74, 31.84, 40.90, 79.45, 115.02, 140.33, 212.11 ppm. - GC/MS (70 eV): *m/z* (%) = 142 (0.3, M^+), 88 (32, $CH_3CH_2COHCHOH^+$), 85 (16, $M^+–C_3H_5O$. - $C_8H_{14}O_2$ (142.2): found C 67.57, H 9.92; calcd. C 67.25, H 10.04.

(4R)-5,5-Dimethyl-4-hydroxy-hept-6-en-3-one [(*R*,*S*)-**5b**]: 88% Yield from hydrazone **4b** after column chromatography (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{RT}$: –152.7 (*c* = 1.0, $CHCl_3$), After HPLC of **4b**. - R_f = 0.38 (diethyl ether/ light petroleum, 1:2). - *ee* = 63% (92% After HPLC of **4b**), determined by ^1H NMR spectroscopy with (–)-1-(9-anthryl)-2,2,2-trifluoroethanol as cosolvent (4 equiv.). - IR (film): ν = 3500 (br, OH), 1700 (s, C=O), 1640 (m, C=C) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.91, 1.14 [s, 6H, $C(CH_3)_2$], 1.05 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 2.38, 2.57 (dq, *J* = 17.9 Hz/ 7.2 Hz, 2H, *H*CHCH$_3$), 3.39 (d, *J* = 6.6 Hz, 1H, OH), 3.94 (d, *J* = 6.3 Hz, 1H, C*H*OH), 5.07 (dd, *J* = 17.3 Hz/ 1.1 Hz, 1H, HC=CHH_{cis}), 5.12 (dd, *J* = 10.7 Hz/ 1.1 Hz, 1H, HC=CHH_{trans}), 5.94 (dd, *J* = 17.3 Hz/ 10.7 Hz, 1H, C*H*=CH$_2$) ppm. - ^{13}C NMR (75 MHz): δ = 7.43, 20.47, 25.38, 35.03, 41.85, 82.66, 113.33, 144.52, 212.87 ppm. - GC/MS (70 eV): *m/z* (%) = 99 (32, $M^+–C_3H_5O^+$), 69 [59, $H_2C=CHC(CH_3)_2^+$], 43 (100). - $C_9H_{16}O_2$ (156.2): calcd. C 69.19, H 10.32; found C 69.42, H 10.75.

(4R,5S)-4-Hydroxy-5-propyl-hept-6-en-3-one [(*R*,*S*)-**5c**]: 92% Yield from hydrazone **4c** after column chromatography (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{RT}$: –119.6 (*c* = 1.3, $CHCl_3$), After HPLC of **4c**. - R_f = 0.46 (diethyl ether/ light petroleum, 1:2). - *syn* = 93% (97% After HPLC of **4c**), determined by ^1H NMR spectroscopy. - *ee* = 84% (98% After HPLC of **4c**), determined by ^1H NMR spectroscopy with (–)-1-(9-anthryl)-2,2,2-trifluorethanol as cosolvent (4 equiv.). - IR (film): ν = 3500 (br, OH), 1710 (s, C=O), 1640 (m, C=C) cm^{-1}. - ^1H NMR (500 MHz): δ = 0.86 (t, *J* = 7.1 Hz, 3H, $CH_2CH_2CH_3$), 1.00-1.45 (m, 4H, $CH_2CH_2CH_3$), 1.13 (t, *J* = 7.2 Hz, 3H, CH_2CH_3), 2.43 (m, 1H, C*H*HC=CH$_2$), 2.47, 2.54 (dqd, *J* = 14.6 Hz/ 7.3 Hz/ 0.7 Hz, 2H, *H*CHCH$_3$), 3.41 (d, *J* = 5.4 Hz, 1H, OH), 4.17 (dd, *J* = 5.4 Hz/ 3.4 Hz), 1H, C*H*OH), 5.13 (m, 2H, HC=CH_2), 5.80 (ddd, *J* = 16.8 Hz/ 10.6 Hz/ 8.9 Hz, 1H, C*H*=CH$_2$) ppm. - ^{13}C NMR (75 MHz): δ = 7.52, 13.92, 20.26, 30.02, 32.08, 47.42, 80.06, 116.52, 138.95, 212.27 ppm. - GC/MS (70 eV): *m/z* (%) = 170 (1.5, M^+), 88 (100, $CH_3CH_2COHCHOH^+$), 85 (16, $M^+–C_3H_5O$). - $C_{10}H_{18}O_2$ (170.3): calcd. C 70.55, H 10.66; found C 70.55, H 10.61.

(2R,3S)-2-Hydroxy-3-methyl-1-phenyl-pent-4-en-1-one [(*R*,*S*)-**5d**]: 98% Yield from hydrazone **4d** after column chromatography (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{RT}$: –17.0 (*c* = 1.3, $CHCl_3$), After HPLC of **4d**. - R_f = 0.49 (diethyl ether/ light petroleum, 1:2). - *syn* = 90% (98% After HPLC of **4d**), determined by

GC (SE-30. 80-10-300): R_t = 11.8 min and ^1H NMR spectroscopy. - *ee* = 90% (92% After HPLC of **4d**), determined by ^1H NMR spectroscopy with (–)-1-(9-anthryl)-2,2,2-trifluoroethanol as cosolvent (4 equiv.). - IR (film): ν = 3500 (br, OH), 1680 (s, C=O), 1640 (m, C=C) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.81 (d, *J* = 6.9 Hz, 3H, $CHCH_3$), 2.68 (m, 1H, $CHCH_3$), 3.72 (d, *J* = 6.6 Hz, 1H, OH), 5.12 (m, 2H, $HC{=}CH_2$), 5.15 (dd, *J* = 6.6 Hz/ 2.5 Hz, 1H, *C*HOH), 6.03 (ddd, *J* = 17.3 Hz/ 10.2 Hz/ 7.1 Hz, 1H, $CH{=}CH_2$), 7.51 (m, 2H, CH_{meta}), 7.62 (m, 1H, CH_{para}), 7.92 (m, 2H, CH_{ortho}) ppm. - ^{13}C NMR (75 MHz): δ = 12.13, 42.01, 76.11, 114.74, 128.50, 128.92, 133.98, 140.61, 201.46 ppm. - GC/MS (70 eV): *m/z* (%) = 190 (1.3, M^+), 136 (43, $C_6H_5COHCHOH^+$), 105 (100, $C_6H_5CO^+$). - $C_{12}H_{14}O_2$ (190.2): calcd. C 75.76, H 7.42; found C = 76.00, H = 7.76.

(2R,3S)-2-Hydroxy-1-phenyl-3-propyl-pent-4-en-1-one [(*R,S*)-**5e**]: 99% Yield from hydrazone **4e** after column chromatography (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{RT}$: –51.1 (*c* = 1.2, $CHCl_3$), After HPLC of **4e**. - R_f = 0.51 (diethyl ether/ light petroleum, 1:2). - *syn* = 94% (96% After HPLC of **4e**), determined by ^1H NMR spectroscopy. - *ee* = 90% (93% After HPLC of **4e**), determined by analytical HPLC and GC employing a chiral stationary phase [3-*O*-acetyl-2,6-dimethyl)-β-cyclodextrin in polysiloxane]. - IR (film): ν = 3500 (br, OH), 1680 (s, C=O), 1640 (m, C=C) cm^{-1}. - ^1H NMR (500 MHz): δ = 0.70 (t, *J* = 7.3 Hz, 3H, CH_3), 0.97, 1.23 (m, 2H, $HCHCH_3$), 1.02, 1.31 (m, 2H, $HCHCH_2CH_3$), 2.46 (m, 1H, $CHHC{=}CH_2$), 3.68 (d, *J* = 5.8 Hz, 1H, OH), 5.10 (d, *J* = 2.7 Hz, 1H, *C*HOH), 5.13 (ddd, *J* = 17.6 Hz/ 1.8 Hz/ 0.8 Hz, 1H, $HC{=}CHH_{cis}$), 5.13 (ddd, *J* = 10.2 Hz/ 1.8 Hz/ 0.5 Hz, 1H, $HC{=}CHH_{trans}$), 5.88 (ddd, *J* = 17.3 Hz/ 10.3 Hz/ 9.2 Hz, 1H, $CH{=}CH_2$), 7.52 (m, 2H, CH_{meta}), 7.63 (m, 1H, CH_{para}), 7.91 (m, 2H, CH_{ortho}) ppm. - ^{13}C NMR (125 MHz): δ = 13.80, 20.12, 29.17, 48.55, 76.86, 116.30, 128.58, 128.97, 128.91, 134.01, 134.27, 139.47, 201.80 ppm. - GC/MS (70 eV): *m/z* (%) = 218 (1.2, M^+), 136 (100, $C_6H_5COHCHOH^+$), 105 (75, $C_6H_5CO^+$). - $C_{14}H_{18}O_2$ (218.3): calcd. C 77.03, H 8.31; found C 76.84, H 8.18.

(R,1'R,2'S)-and (S,1'R,2'S)-Methoxyphenyl-acetic acid 1-(2-ethyl-[1,3]-dioxolan-2-yl)-2-methyl-but-3-enyl ester [(*R,R,S*)-*6*, (*S,R,S*)-**6**]: Ketone **5a** (0.42 mmol) was dissolved in ethane-1,2-diol (2.1 mmol) and benzene (10 ml) and heated to reflux together with PPTS (20 mol%) with azeotropic water removal by a Dean stark trap until complete conversion of the starting ketone (TLC control). After evaporation of the solvent, the residue was diluted with diethyl ether and washed once with saturated $NaHCO_3$ solution and brine. Drying over $MgSO_4$, evaporation of the solvent and purification by column chromatography (diethyl ether/ light petroleum, 1:2) afforded (1*R*,2*S*)-1-(2-ethyl-[1,3]-dioxolan-2-yl)-2-methyl-but-3-en-1-ol as a colourless liquid (80% yield). The alcohol was converted to the corresponding (*R*)- and (*S*)-MPA ester **6** according to literature procedure[17]. - 96% Yield after purification by column chromatography (diethyl ether/ light petroleum, 1:4). - R_f = 0.39 [(*R,R,S*)-**6**], 0.28 [(*S,R,S*)-**6**] (diethyl ether/ light petroleum, 1:2). - IR (film): ν = 1750 (s, C=0), 1640 (w, C=C), 1110 (s, COC) cm^{-1}. - ^1H NMR (500 MHz): (*R,R,S*)-**6**: δ = 0.74 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 0.99 (d, *J* = 6.8 Hz, 3H, $CHCH_3$), 1.52 (q, *J* = 7.5 Hz, 2H, CH_2CH_3), 2.54 (m, 1H, $CHCH_3$), 3.39 (m, 1H, OC*H*HCHHO), 3.42 (s, 3H, OCH_3), 3.63 (m, 2H, OCH*H*CH*H*O), 3.75 (m, 1H, OCHHC*H*HO), 4.75 (s, 1H, $CHOCH_3$), 4.95 (ddd, *J* = 10.3 Hz/ 1.6 Hz/ 1.0 Hz, 1H, $HC{=}CHH_{trans}$), 4.96 (d, *J* = 6.1 Hz, 1H, CHOCO), 4.98 (dt, *J* = 16.9 Hz/ 1.5 Hz, 1H, $HC{=}CHH_{cis}$), 5.78 (ddd, *J* = 17.1 Hz/ 10.3 Hz/ 7.6 Hz, 1H, $HC{=}CH_2$), 7.29-7.38 (m, 3H, CH_{meta}, CH_{para}), 7.46 (m, 2H, CH_{ortho}) ppm; (*S,R,S*)-**6**: δ = 0.65 (d, *J* = 6.8 Hz, 3H, $CHCH_3$), 0.89 (t, *J* = 7.4 Hz, 3H, CH_2CH_3), 1.67 (m, 1H, $CHHCH_3$), 1.74 (m, 1H, $CHHCH_3$), 2.40

(m, 1H, C*H*CH$_3$), 3.43 (s, 3H, OCH$_3$), 3.88 (m, 2H, OC*H*HC*H*HO), 3.94 (m, 2H, OCH*H*CH*H*O), 4.77 (s, 1H, C*H*OCH$_3$), 4.82 (ddd, *J* = 17.0 Hz/ 1.6 Hz/ 1.1 Hz, 1H, HC=CH*H*$_{cis}$), 4.84 (ddd, *J* = 10.5 Hz/ 1.6 Hz/ 0.9 Hz, 1H, HC=CH*H*$_{trans}$), 4.90 (d, *J* = 6.7 Hz, 1H, CHOCO), 5.61 (ddd, *J* = 17.0 Hz/ 10.5 Hz/ 7.9 Hz, 1H, *H*C=CH$_2$), 7.25-7.38 (m, 3H, CH$_{meta}$, CH$_{para}$), 7.44 (m, 2H, CH$_{ortho}$) ppm. - ^{13}C NMR (125 MHz) [(*R*)-**6**]: δ = 6.79, 15.65, 27.58, 38.28, 57.39, 65.51, 65.65, 77.30, 82.83, 110.83, 113.84, 127.68, 128.53, 128.78 (C-14), 136.28, 140.95, 170.11 ppm. - GC/MS (70 eV) [(*R*)-**6**]: *m*/*z* (%) = 305 (1.2, M$^+$-CH$_2$CH$_3$), 121 (29, $C_6H_5CHOCH_3^+$), 101 [100, C(OCH$_2$CH$_2$O)CH$_2$CH$_3^+$]. - $C_{19}H_{26}O_5$ (404.3): calcd. C 68.24, H 7.84; found C 68.56, H 7.99.

(S)-1-[2-((E)-(But-2-enyloxy)-1-ethylidenamino]-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S*)-**7a**]: 85% Yield from (*E*)-(but-2-enyloxy)-acetaldehyde after column chromatography (diethyl ether/ light petroleum, 1:6). - $[\alpha]_D^{RT}$: +4.94 ° (neat). - R_f = 0.12 (diethyl ether/ light petroleum, 1:6). - $(E)_{CC}$ = 96%, Determined by GC. - IR (film): ν = 1670 (w, C=C), 1595 (m, C=N), 1090 (s, COC) cm^{-1}. - ^{1}H NMR (300 MHz): δ = 0.86, 0.88 [t, *J* = 7.4 Hz, 6H, C(CH$_2$C*H*$_3$)$_2$], 1.40-2.10 [m, 11H, 4 ring-CH$_2$, 4 C(C*H*$_2$CH$_3$)$_2$, CHC*H*$_3$], 2.80 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH$_3$), 3.32 (m, 1H, HC*H*N), 3.61 (dd, *J* = 9.1 Hz/ 2.7 Hz, 1H, CHN), 3.93 (m, 2H, CHC*H*$_2$O), 4.03 (d, *J* = 5.7 Hz, 2H, OC*H*$_2$CHN), 5.60 (m, 1H, C*H*CH$_2$O), 5.72 (dqt, *J* = 15.2 Hz, 6.1 Hz/ 1.0 Hz, 1H, C*H*CH$_3$), 6.51 (t, *J* = 5.4 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.85, 8.47, 17.78, 23.76, 24.50, 26.26, 50.40, 50.67, 68.55, 70.62, 70.63, 80.41, 127.61, 129.63, 129.66 ppm. - GC/MS (70 eV): *m*/*z* (%) = 282 (1.4, M$^+$), 181 [100, M$^+$–H$_3$COC(C$_2$H$_5$)$_2$], 70 (18, $C_4H_8N^+$), 55 (70, CH$_3$HCCHCH$_2^+$). - $C_{16}H_{30}N_2O_2$ (282.4): calcd. C 68.04, H 10.71, N 9.92; found C 68.10, H 11.08, N 9.78.

(S)-2-(1-Ethyl-1-methoxypropyl)-1-[2-(3-methyl-but-2-enyloxy)-1-ethylidenamino]-pyrrolidine [(*S*)-**7b**]: 98% Yield from (3-methyl-but-2-enyloxy)-acetaldehyde after column chromatography (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{RT}$: +9.00 ° (neat). - R_f = 0.26 (diethyl ether/ light petroleum, 1:4). - IR (film): ν = 1670 (w, C=C), 1595 (m, C=N), 1080 (s, COC) cm^{-1}. - ^{1}H NMR (300 MHz): δ = 0.86, 0.88 [t, *J* = 7.4 Hz, 6H, C(CH$_2$C*H*$_3$)$_2$], 1.40-2.05 [m, 8H, 4 ring-CH$_2$, 4 C(C*H*$_2$CH$_3$)$_2$], 1.68 [s, 3H, C(CH$_3$)$_{cis}$], 1.75 [s, 3H, C(CH$_3$)$_{trans}$], 2.80 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH$_3$), 3.33 (m, 1H, HC*H*N), 3.61 (dd, *J* = 9.1 Hz/ 2.7 Hz, 1H, CHN), 3.98 (d, *J* = 6.5 Hz, 2H, CHC*H*$_2$O), 4.03 (d, *J* = 5.4 Hz, 2H, OC*H*$_2$CHN), 5.38 (m, 1H, C*H*CH$_2$O) 6.53 (t, *J* = 5.4 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.85, 8.46, 18.03, 23.78, 24.52, 26.27, 25.80, 50.40, 50.71, 66.30, 68.59, 70.72, 80.41, 121.22, 129.85, 136.88 ppm. - GC/MS (70 eV): *m*/*z* (%) = 296 (1.6, M$^+$), 195 [100, M$^+$–H$_3$COC(C$_2$H$_5$)$_2$], 69 (64, (CH$_3$)$_2$CCHCH$_2^+$). - $C_{17}H_{32}N_2O_2$ (296.4): calcd. C 68.88, H 10.88, N 9.45; found C 68.91, H 10.64, N 9.16.

(S)-2-(1-Ethyl-1-methoxypropyl)-1-[2-((E)-pent-2-enyloxy)-1-ethylidenamino]-pyrrolidine [(*S*)-**7c**]: 92% Yield from (*E*)-(pent-2-enyloxy)-acetaldehyde after column chromatography (diethyl ether/ light petroleum, 1:4). - $[\alpha]_D^{RT}$: +19.8 (*c* = 1.1, CHCl$_3$). - R_f = 0.20 (diethyl ether/ light petroleum, 1:4). - $(E)_{CC}$ = 97%, Determined by GC and ^{13}C NMR spectroscopy. - IR (film): ν = 1670 (w, C=C), 1595 (m, C=N), 1090 (s, COC) cm^{-1}. - ^{1}H NMR (300 MHz): δ = 0.86, 0.88 [t, *J* = 7.4 Hz, 6H, C(CH$_2$C*H*$_3$)$_2$], 1.40-2.10 [m, 10H, 4 ring-CH$_2$, 4H C(C*H*$_2$CH$_3$)$_2$, 2 CHC*H*$_2$CH$_3$], 2.80 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH$_3$), 3.33 (m, 1H, HC*H*N), 3.61 (dd, *J* = 9.1 Hz/ 2.7 Hz, 1H, CHN), 3.96 (m, 2H, CHC*H*$_2$O), 4.04 (d, *J* = 5.4 Hz, 2H, OC*H*$_2$CHN), 5.58 (dtt, *J* = 15.6 Hz/ 6.7 Hz/, 1.7 Hz, 1H, C*H*CH$_2$O), 5.76 (dtt, *J* = 15.3 Hz, 6.1 Hz/ 1.0 Hz,

1H, C*H*CH_2CH_2), 6.52 (t, $J = 5.4$ Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.85, 8.48, 13.32, 23.76, 24.51, 26.27, 25.32, 50.40, 50.66, 68.55, 70.64, 70.70, 80.39, 125.25, 129.63, 136.43 ppm. - GC/MS (70 eV): *m/z* (%) = 296 (1.9, M^+), 195 [100, $M^+-H_3COC(C_2H_5)_2$], 69 (45, $CH_3CH_2HCCHCH_2^+$). - $C_{17}H_{32}N_2O_2$ (296.4): calcd. C 68.88, H 10.88, N 9.45; found C 68.81, H 10.92, N 9.09.

(S)-2-(1-Ethyl-1-methoxypropyl)-1-[2-((E)-hex-2-enyloxy)-1-ethylidenamino]-pyrrolidine [(*S*)-**7d**]: 93% Yield from (*E*)-(hex-2-enyloxy)-acetaldehyde after column chromatography (diethyl ether/ light petroleum, 1:7). - $[\alpha]_D^{RT}$: +3.30 °(neat). - R_f = 0.21 (diethyl ether/ light petroleum, 1:7). - $(E)_{CC}$ > 97%, Determined by ^{13}C NMR spectroscopy. - IR (film): ν = 1670 (w, C=C), 1595 (m, C=N), 1080 (s, COC) cm^{-1}. - ^{1}H NMR (300 MHz): δ = 0.86, 0.88, 0.91 [t, $J = 7.4$ Hz, 9H, 6 $C(CH_2CH_3)_2$, 3 $CHCH_2CH_2CH_3$], 1.41 (m, 2H, $CH_2CH_2CH_3$), 1.46-2.10 [m, 10H, 4 Ring-CH_2, 4 $C(CH_2CH_3)_2$, 2 $CHCH_2CH_2CH_3$], 2.80 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH_3), 3.33 (m, 1H, HC*H*N), 3.62 (dd, $J = 9.1$ Hz/ 2.4 Hz, 1H, CHN), 3.94 (d, $J = 5.8$ Hz, 2H, $CHCH_2O$), 4.04 (d, $J = 5.4$ Hz, 2H, OCH_2CHN), 5.57 (dtt, $J = 15.3$ Hz/ 6.1 Hz/, 1.4 Hz, 1H, C*H*CH_2O), 5.70 (dtt, $J = 15.6$ Hz/ 6.5 Hz/ 1.0 Hz, 1H, C*H*CH_2CH_2), 6.51 (t, $J = 5.4$ Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.84, 8.47, 13.71, 22.23, 23.73, 23.77, 24.50, 26.27, 34.42, 50.40, 50.66, 68.54, 70.55, 70.68, 80.39, 126.38, 129.62, 136.78 ppm. - GC/MS (70 eV): *m/z* (%) = 310 (1.8, M^+), 209 [100, $M^+-H_3COC(C_2H_5)_2$], 127 (25, $OCH_2CHNNC_4H_8^+$). - $C_{18}H_{34}N_2O_2$ (310.5): calcd. C 69.63, H 11.04, N 9.02; found C 69.76, H 11.33, N 8.98.

(S)-2-(1-Ethyl-1-methoxypropyl)-1-[2-((E)-4-methyl-pent-2-enyloxy)-1-ethylidenamino]-pyrrolidine [(*S*)-**7e**]: 92% Yield from (*E*)-(4-methyl-pent-2-enyloxy)-acetaldehyde after column chromatography (diethyl ether/ light petroleum, 1:6). - $[\alpha]_D^{RT}$: +22.7 (c = 1.0, $CHCl_3$). - R_f = 0.23 (diethyl ether/ light petroleum, 1:6). - $(E)_{CC}$ > 97%, Determined by ^{13}C NMR spectroscopy. - IR (film): ν = 1665 (w, C=C), 1595 (m, C=N), 1085 (s, COC) cm^{-1}. - ^{1}H NMR (300 MHz): δ = 0.86, 0.88, [t, $J = 7.4$ Hz, 6H, $C(CH_2CH_3)_2$], 1.00 [t, $J = 6.8$ Hz, 6H, $CH(CH_3)_2$], 1.40-2.10 [m, 8H, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.30 [m, 1H, $CH(CH_3)_2$], 2.80 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH_3), 3.33 (m, 1H, HC*H*N), 3.61 (dd, $J = 9.1$ Hz/ 2.4 Hz, 1H, CHN), 3.94 (d, $J = 6.4$ Hz, 2H, $CHCH_2O$), 4.04 (d, $J = 5.4$ Hz, 2H, OCH_2CHN), 5.53 (dtd, $J = 15.6$ Hz/ 7.2 Hz/, 1.2 Hz, 1H, C*H*CH_2O), 5.69 (ddt, $J = 15.6$ Hz/ 6.4 Hz/ 1.0 Hz, 1H, C*H*CH_2CH_2), 6.52 (t, $J = 5.4$ Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.84, 8.48, 22.19, 23.75 24.50, 26.27, 30.78, 50.40, 50.65, 68.54, 70.62, 70.77, 80.38, 123.27, 129.62, 141.70 ppm. - GC/MS (70 eV): *m/z* (%) = 310 (0.7, M^+), 209 [100, $M^+-H_3COC(C_2H_5)_2$], 127 (51, $OCH_2CHNNC_4H_8^+$). - $C_{18}H_{34}N_2O_2$ (310.5): calcd. C 69.63, H 11.04, N 9.02; found C 69.62, H 11.15, N 8.78.

(S)-2-(1-Ethyl-1-methoxypropyl)-1-[2-((E)-hept-2-enyloxy)-1-ethylidenamino]-pyrrolidine [(*S*)-**7f**]: 48% Yield from (*E*)-(hept-2-enyloxy)-acetaldehyde after column chromatography (diethyl ether/ light petroleum, 1:8). - $[\alpha]_D^{RT}$: +4.17 ° (neat). - R_f = 0.55 (diethyl ether/ light petroleum, 1:2). - $(E)_{CC}$ > 97%, Determined by ^{13}C NMR spectroscopy. - IR (film): ν = 1670 (w, C=C), 1595 (m, C=N), 1090 (s, COC) cm^{-1}. - ^{1}H NMR (300 MHz): δ = 0.86, 0.88, [t, $J = 7.4$ Hz, 6H, $C(CH_2CH_3)_2$], 0.89 [t, $J = 7.1$ Hz, 3H, $(CH_2)_3CH_3$], 1.20-2.10 [m, 14H, 6 $(CH_2)_3CH_3$, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.80 (m, 1H, *H*CHN), 3.24 (s, 3H, OCH_3), 3.32 (m, 1H, HC*H*N), 3.62 (dd, $J = 9.1$ Hz/ 2.4 Hz, 1H, CHN), 3.94 (m, 2H, $CHCH_2O$), 4.03 (d, $J = 5.4$ Hz, 2H, OCH_2CHN), 5.57 (dtt, $J = 15.4$ Hz/ 6.1 Hz/, 1.4 Hz, 1H, C*H*CH_2O), 5.71 (dtt, $J = 15.4$ Hz, 6.4 Hz/ 1.0

Hz, 1H, C*H*CH$_2$CH$_2$), 6.52 (t, *J* = 5.4 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.85, 8.48, 13.94, 22.25, 23.75 24.50, 26.27, 31.25, 32.02, 50.40, 50.69, 68.58, 70.58, 70.72, 80.44, 126.21, 129.69, 135.09 ppm. - GC/MS (70 eV): *m/z* (%) = 324 (1.5, M$^+$), 223 [100, M$^+$-H$_3$COC(C$_2$H$_5$)$_2$], 127 (27, OCH$_2$CHNNC$_4$H$_8$$^+$). - $C_{19}H_{36}N_2O_2$ (324.5): calcd. C 70.32, H 11.18, N 8.63; found C 70.27, H 11.66, N 8.83.

(S)-2-(1-Ethyl-1-methoxypropyl)-1-[2-((E)-5-methyl-hex-2-enyloxy)-1-ethylidenamino]-pyrrolidine [(*S*)-**7g**]: 92% Yield from (*E*)-(5-methyl-hex-2-enyloxy)-acetaldehyde after column chromatography (diethyl ether/ light petroleum, 1:7). - $[\alpha]_D^{RT}$: +3.12 ° (neat). - R_f = 0.44 (diethyl ether/ light petroleum, 1:4). - $(E)_{CC}$ = 95%, Determined by ^{13}C NMR spectroscopy. - IR (film): ν = 1670 (w, C=C), 1595 (m, C=N), 1090 (s, COC) cm^{-1}. - ^{1}H NMR (300 MHz): δ = 0.86, 0.88, [t, *J* = 7.4 Hz, 6H, C(CH$_2$C*H*$_3$)$_2$], 0.89 [d, *J* = 6.7 Hz, 6H, CH(CH$_3$)$_2$], 1.40-2.10 [m, 10H, 4 Ring-CH$_2$, 4 C(C*H*$_2$CH$_3$)$_2$, 2 (CH$_3$)$_2$CHC*H*$_2$], 2.80 (m, 1H, *H*CHN), 3.24 (s, 3H, OCH$_3$), 3.33 (m, 1H, HC*H*N), 3.62 (dd, *J* = 9.4 Hz/ 2.4 Hz, 1H, CHN), 3.96 (d, *J* = 6.7 Hz, 2H, CHC*H*$_2$O), 4.03 (d, *J* = 5.4 Hz, 2H, OC*H*$_2$CHN), 5.56 (dtt, *J* = 15.4 Hz/ 6.4 Hz/ 1.3 Hz, 1H, C*H*CH$_2$O), 5.68 [m, 1H, C*H*CH$_2$CH(CH$_3$)$_2$], 6.52 (t, *J* = 5.4 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.85, 8.48, 22.34, 23.74, 23.77, 24.50, 26.28, 28.22, 41.74, 50.43, 50.67, 68.57, 70.50, 70.64, 80.42, 127.45, 129.66, 133.69 ppm. - GC/MS (70 eV): *m/z* (%) = 324 (3.0, M$^+$), 223 [100, M$^+$–H$_3$COC(C$_2$H$_5$)$_2$], 127 (29, OCH$_2$CHNNC$_4$H$_8$$^+$). - $C_{19}H_{36}N_2O_2$ (324.5): calcd. C 70.32, H 11.18, N 8.63; found C 70.38, H 11.54, N 8.90.

(2S,2´R,3´S)-2-(1-Ethyl-1-methoxypropyl)-1-(2´-hydroxy-3´-methyl-1´-pent-4´-enylidenamino)-pyrrolidine [(*S,R,S*)-**8a**]: 86% Yield from hydrazone (*S*)-**7a** after column chromatography (diethyl ether/ light petroleum, 1:2). - R_f = 0.19 (diethyl ether/ light petroleum, 1:2). - *syn* = 95%, Determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 91%, Determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 3350 (br, OH), 1640 (w, C=C), 1600 (m, C=N) cm^{-1}. - ^{1}H NMR (300 MHz): δ = 0.87, 0.91 [t, *J* = 7.8 Hz, 6H, C(CH$_2$C*H*$_3$)$_2$], 1.07 (d, *J* = 7.1 Hz, 3H, CHC*H*$_3$), 1.40-2.05 [m, 8H, 4 ring-CH$_2$, 4 C(C*H*$_2$CH$_3$)$_2$], 2.34 (m, 1H, C*H*CH$_3$), 2.71 (m, 1H, *H*CHN), 3.25 (s, 3H, OCH$_3$), 3.30-3.65 (m, 3H, HC*H*N, CHN; OH), 4.11 (dd, *J* = 5.8 Hz/ 2.4 Hz, 1H, C*H*OH), 5.09 (m, 2H, HC=C*H*$_2$), 5.83 (ddd, *J* = 17.3 Hz/ 10.1 Hz/ 7.4 Hz, 1H, *H*C=CH$_2$), 6.57 (d, *J* = 2.7 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.82, 8.59, 15.01, 23.74, 24.58, 26.69, 43.65, 50.44, 51.57, 68.72, 73.85, 80.23, 114.97, 133.56, 140.41 ppm. - GC/MS (70 eV): *m/z* (%) = 181 [55, M$^+$–H$_3$COC(C$_2$H$_5$)$_2$], 70 (100, C$_4$H$_8$N$^+$). - $C_{16}H_{30}N_2O_2$ (282.4): C 68.04, H 10.71, N 9.92; found C 67.74, H 11.14, N 9.88.

(2S,2´R)-1-(3´,3´-Dimethyl-2´-hydroxy-1´-pent-4´-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*R*)-**8b**]: 72% Yield from hydrazone (*S*)-**7b** after column chromatography (diethyl ether/ light petroleum, 1:2). - R_f = 0.34 (diethyl ether/ light petroleum, 1:2). - *de* = 81%, Determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 3450 (br, OH), 1640 (w, C=C), 1600 (m, C=N) cm^{-1}. - ^{1}H NMR (300 MHz): δ = 0.87, 0.90 [t, *J* = 7.5 Hz, 6H, C(CH$_2$C*H*$_3$)$_2$], 1.00, 1.07 [s, 6H, C(CH$_3$)$_2$], 1.40-2.10 [m, 8H, 4 ring-CH$_2$, 4 C(C*H*$_2$CH$_3$)$_2$], 2.69 (m, 1H, *H*CHN), 3.29 (s, 3H, OCH$_3$), 3.35 (m, 1H, HC*H*N), 3.57 (dd, *J* = 9.3 Hz/ 2.7 Hz, 1H, CHN), 3.71 (s, 1H, OH), 3.95 (d, *J* = 2.0 Hz, 1H, C*H*OH), 5.06 (m, 2H, HC=C*H*$_2$), 5.89 (dd, *J* = 17.0 Hz/ 11.2 Hz, 1H, *H*C=CH$_2$), 6.57 (d, *J* = 2.7 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.82,

8.60, 21.61, 23.41, 23.69, 23.72, 24.55, 26.28, 41,55, 50.44, 51.59, 68.74, 76.96, 80.17, 112.56, 132.71, 144.99 ppm. - GC/MS (70 eV): *m/z* (%) = 195 [100, M^+–$H_3COC(C_2H_5)_2$], 70 (53, $C_4H_8N^+$). - $C_{17}H_{32}N_2O_2$ (296.5): calcd. C 68.88,, H 10.88, N 9.45; found C 68.96, H 11.09, N 9.54.

(2S,2´R,3´S)-1-(3´-Ethyl-2´-hydroxy-1´-pent-4´-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R,S*)-**8c**]: 81% Yield from hydrazone (*S*)-**7c** after column chromatography (diethyl ether/ light petroleum, 1:2). - R_f = 0.24 (diethyl ether/ light petroleum, 1:2). - *syn* = 92%, Determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 92%, Determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 3450 (br, OH), 1640 (w, C=C), 1600 (m, C=N) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.84-0.94 [m, 9H, 3 CH_2CH_3, 6 $C(CH_2CH_3)_2$], 1.20-2.10 [m, 11H, 2 CH_2CH_3, $CHCH_2$, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.71 (m, 1H, *H*CHN), 3.25 (s, 3H, OCH_3), 3.30-3.65 (m, 3H, HC*H*N, CHN; OH), 4.15 (dd, *J* = 6.4 Hz/ 2.7 Hz, 1H, C*H*OH), 5.09 (m, 2H, HC=CH_2), 5.65 (ddd, *J* = 17.3 Hz/ 10.5 Hz/ 9.2 Hz, 1H, *H*C=CH_2), 6.57 (d, *J* = 3.1 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.82, 8.60, 11.64, 22.82, 23.72, 23.75, 24.55, 26.27, 50.45, 51.56, 52.38, 68.70, 72.97, 80.22, 116.98, 133.78, 138.60 ppm. - GC/MS (70 eV): *m/z* (%) = 296 (0.2, M^+), 195 [81, M^+–$H_3COC(C_2H_5)_2$], 177 (100, 195–H_2O). - $C_{17}H_{32}N_2O_2$ (296.5): calcd. C 68.88, H 10.88, N 9.45; found C 68.55, H 10.93, N 9.12.

(2S,2´R,3´S)-2-(1-Ethyl-1-methoxypropyl)-1-(2´-hydroxy-3´-propyl-1´-pent-4´-enylidenamino)-pyrrolidine [(*S,R,S*)-**8d**]: 91% Yield from hydrazone (*S*)-**7d** after column chromatography (diethyl ether/ light petroleum, 1:2). - R_f = 0.32 (diethyl ether/ light petroleum, 1:2). - *syn* = 92%, Determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 92%, Determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 3450 (br, OH), 1640 (w, C=C), 1600 (m, C=N) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.87, 0.90 [t, *J* = 7.4 Hz, 6H, $C(CH_2CH_3)_2$], 0.90 (t, *J* = 7.5 Hz, 3H, CH_2CH_3), 1.10-2.10 [m, 12H, 4 $CH_2CH_2CH_3$, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.18 (m, 1H, C*H*CH_2), 2.70 (m, 1H, *H*CHN), 3.25 (s, 3H, OCH_3), 3.36 (m, 1H, HC*H*N), 3.50-3.65 (m, 2H, CHN; OH), 4.12 (dd, *J* = 6.4 Hz/ 2.7 Hz, 1H, C*H*OH), 5.09 (m, 2H, HC=CH_2), 5.57 (ddd, *J* = 17.0 Hz/ 10.5 Hz/ 9.1 Hz, 1H, *H*C=CH_2), 6.57 (d, *J* = 2.7 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.82, 8.59, 14.12, 20.21, 23.71, 23.75, 24.55, 26.26, 32.13, 50.31, 50.45, 51.56, 68.69, 73.15, 80.23, 116.77, 133.69, 138.89 ppm. - GC/MS (70 eV): *m/z* (%) = 209 [100, M^+–$H_3COC(C_2H_5)_2$], 70 (89, $C_4H_8N^+$). - $C_{18}H_{34}N_2O_2$ (310.5): calcd. C 69.63, H = 11.04, N 9.02; found C 69.70, H 11.51, N 9.25.

(2S,2´R,3´S)-2-(1-Ethyl-1-methoxypropyl)-1-(2´-hydroxy-3´-isopropyl-1´-pent-4´-enylidenamino)-pyrrolidine [(*S,R,S*)-**8e**]: 91% Yield from hydrazone (*S*)-**7e** after column chromatography (diethyl ether/ light petroleum, 1:2). - R_f = 0.24 (diethyl ether/ light petroleum, 1:2). - *syn* = 87%, Determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 91%, Determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 3450 (br, OH), 1640 (w, C=C), 1600 (m, C=N) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.85-0.95 [m, 12H, 6 $CH(CH_3)_2$, 6 $C(CH_2CH_3)_2$], 1.40-2.20 [m, 10H, C*H*$CH(CH_3)_2$, C*H*$(CH_3)_2$, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.69 (m, 1H, *H*CHN), 3.25 (s, 3H, OCH_3), 3.33 (m, 1H, HC*H*N), 3.58 (dd, *J* =6.1 Hz/ 3.1 Hz, 1H, CHN), 3.71 (s, 1H, OH), 4.24 (dd, *J* = 8.1 Hz/ 3.1 Hz, 1H, C*H*OH), 5.06 (ddd, *J* = 17.3 Hz/ 2.4 Hz/ 0.7 Hz, 1H, HC=CHH_{cis}), 5.17 (dd, *J* = 10.5 Hz/ 2.0 Hz, 1H, HC=CHH_{trans}), 5.61 (ddd, *J* = 17.0 Hz/ 10.2 Hz/ 9.8 Hz, 1H, *H*C=CH_2), 6.56 (d, *J* = 3.1 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.82, 8.60, 13.38, 21.17, 23.69, 23.75, 24.54, 26.26, 27.19, 50.45, 51.51, 57.16, 68.68, 70.54, 80.25, 118.51, 134.27, 135.58 ppm. - GC/MS (70 eV): *m/z* (%) = 310 (0.7,

M^+), 209 [72, $M^+–H_3COC(C_2H_5)_2$], 70 (100, $C_4H_8N^+$). - $C_{18}H_{34}N_2O_2$ (310.5): calcd. C 69.63, H = 11.04, N 9.02; found C 69.13, H 11.07, N 9.51.

(2S,2´R,3´S)-1-(3´-Butyl-2´-hydroxy-1´-pent-4´-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R,S*)-**8f**]: 89% Yield from hydrazone (*S*)-**7f** after column chromatography (diethyl ether/ light petroleum, 1:4). - R_f = 0.27 (diethyl ether/ light petroleum, 1:4). - *syn* = 90%, Determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 90%, Determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 3450 (br, OH), 1640 (w, C=C), 1600 (m, C=N) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.82-0.94 [m, 9H, $C(CH_2CH_3)_2$, $CH_2CH_2CH_3$], 1.10-2.08 [m, 14H, 6 $CH_2CH_2CH_2CH_3$, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.15 (m, 1H, $CHCH_2$), 2.70 (m, 1H, *H*CHN), 3.25 (s, 3H, OCH_3), 3.36 (m, 1H, HC*H*N), 3.45-3.65 (m, 2H, CHN; OH), 4.13 (dd, *J* = 6.4 Hz/ 2.7 Hz, 1H, *C*HOH), 5.10 (m, 2H, $HC{=}CH_2$), 5.65 (ddd, *J* = 17.1 Hz/ 10.4 Hz/ 9.4 Hz, 1H, *H*C=CH_2), 6.57 (d, *J* = .3.0 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.84, 8.60, 14.09, 22.80, 23.77, 24.60, 26.30, 29.38, 29.68, 50.47, 50.61, 51.61, 68.76, 73.23, 80.29, 116.83, 133.78, 139.04 ppm. - MS (70 eV): *m/z* (%) = 324 (0.8, M^+), 223 [100, $M^+–H_3COC(C_2H_5)_2$], 70 (31, $C_4H_8N^+$). - $C_{19}H_{36}N_2O_2$ (324.5): calcd. C 70.32, H 11.18, N 8.63; found C 70.34, H 11.20, N 9.16.

(2S,2´R,3´S)-2-(1-Ethyl-1-methoxypropyl)-1-(2´-hydroxy-3´-isobutyl-1´-pent-4´-enylidenamino)-pyrrolidine [(*S,R,S*)-**8g**]: 81% Yield from hydrazone (*S*)-**7g** after column chromatography (diethyl ether/ light petroleum, 1:4). - R_f = 0.20 (diethyl ether/ light petroleum, 1:4). - *syn* = 88%, Determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 90%, Determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 3450 (br, OH), 1640 (w, C=C), 1600 (m, C=N) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.85, 0.91 [d, *J* = 6.6 Hz, 6H, $CH(CH_3)_2$], 0.87, 0.90 [t, *J* = 7.4 Hz, 6H, $C(CH_2CH_3)_2$], 1.10-2.10 [m, 11H, $CH(CH_3)_2$, 2 $CHCH_2$, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.27 (m, 1H, *C*HHC=CH_2), 2.70 (m, 1H, *H*CHN), 3.25 (s, 3H, OCH_3), 3.35 (m, 1H, HC*H*N), 3.45-3.65 (m, 2H, CHN; OH), 4.10 (dd, *J* = 6.4 Hz/ 3.0 Hz, 1H, *C*HOH), 5.10 (m, 2H, $HC{=}CH_2$), 5.65 (ddd, *J* = 16.8 Hz/ 10.7 Hz/ 9.4 Hz, 1H, *H*C=CH_2), 6.57 (d, *J* = 2.7 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = 7.84, 8.58, 21.43, 23.90, 25.13, 23.76, 24.58, 26.28, 39.13, 48.40, 50.47, 51.63/ 51.36, 68.76, 73.48, 80.28, 116.72, 133.66, 139.08 ppm. - GC/MS (70 eV): *m/z* (%) = 324 (0.8, M^+), 223 [100, $M^+–H_3COC(C_2H_5)_2$], 70 (36, $C_4H_8N^+$). - $C_{19}H_{36}N_2O_2$ (324.5): calcd. C 70.32, H 11.18, N 8.63; found C 70.09, H 11.40, N 9.05.

(2S,2´R,3´S)-1-(2´-tert-Butyldimethylsilyloxy-3´-methyl-1´-pent-4´-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R,S*)-**9a**]: 93% Yield from hydrazone **8a** after column chromatography (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - $[\alpha]_D^{RT}$: +32.6 (c = 1.0, $CHCl_3$), After HPLC (diethyl ether/ light petroleum, 3:97, flow: 18 ml/ min, R_t = 21.3 min). - R_f = 0.19 (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - *syn* = 95% (>98% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 91% (> 98% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 1640 (w, C=C), 1595 (m, C=N), 1070 (s, SiOC) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.01, 0.06 [s, 6H, $Si(CH_3)_2$], 0.83-0.91 [m, 15H, 9 ($C(CH_3)_3$, 6 $C(CH_2CH_3)_2$], 1.03 (d, *J* = 6.8, 3H, $CHCH_3$), 1.40-2.05 [m, 8H, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.39 (m, 1H, $CHCH_3$), 2.74 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH_3), 3.28 (m, 1H, HC*H*N), 3.54 (dd, *J* = 6.4 Hz/ 2.4 Hz, 1H, CHN), 3.98 (t, *J* = 6.4 Hz, 1H, CHOSi), 4.99 (m, 2H, $HC{=}CH_2$), 5.85 (m, 1H, *H*C=CH_2), 6.32 (d, *J* = 6.4 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = –4.72, –3.81, 7.80, 8.54, 15.26, 18.23, 23.72, 23.76, 24.63, 26.24, 25.94, 43.82, 50.37, 50.75, 68.47, 77.37, 80.39, 114.05, 136.13, 140.89 ppm.

- GC/MS (70 eV): *m/z* (%) = 341 [6, M^+–H_2C=$CHCH(CH_3)$], 295 [100, M^+–$H_3COC(C_2H_5)_2$], 70 (18, $C_4H_8N^+$). - $C_{22}H_{44}N_2O_2Si$ (396.7): calcd. C 66.61, H 11.18, N 7.06; found C 66.57, H 11.25, N 7.55.

(2S,2'R)-1-(2'-tert-Butyldimethylsilyloxy-3',3'-dimethyl-1'-pent-4'-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R*)-**9b**]: 94% Yield from hydrazone **8b** after column chromatography (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - $[\alpha]_D^{RT}$: +11.3 (c = 1.0, $CHCl_3$), After HPLC (diethyl ether/ light petroleum, 5:95, flow: 10 ml/ min, R_t = 17.3 min). - R_f = 0.28 (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - *de* = 81% (> 98% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 1640 (w, C=C), 1595 (m, C=N), 1070 (s, SiOC) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.07 [s, 6H, $Si(CH_3)_2$], 0.86-0.94 [m, 15H, 9 ($C(CH_3)_3$, 6 $C(CH_2CH_3)_2$], 1.01, 1.05 [s, 6H, $C(CH_3)_2$], 1.45-2.05 [m, 8H, 4 ring-CH_2, 4 $C(CH_2CH_3)_2$], 2.76 (m, 1H, *H*CHN), 3.27 (s, 3H, OCH_3), 3.30 (m, 1H, HC*H*N), 3.57 (dd, *J* = 8.8 Hz/ 3.4 Hz, 1H, CHN), 3.83 (d, *J* = 7.1 Hz, 1H, CHOSi), 4.97 (dd, *J* = 17.3 Hz/ 1.7 Hz, 1H, HC=CCHH_{cis}) 4.99 (dd, *J* = 10.9 Hz/ 1.7 Hz, 1H, HC=CCHH_{trans}), 6.01 (dd, *J* = 17.3 Hz/ 11.1 Hz, 1H, *H*C=CH_2), 6.33 (d, *J* = 7.5 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = –4.89, –3.53, 7.79, 8.58, 18.20, 22.71, 23.97, 23.72, 23.77, 24.65, 26.24, 25.93, 41.89, 50.37, 50.62, 68.50, 80.39, 80.73, 111.38, 135.42, 145.49 ppm. - MS (70 eV): *m/z* (%) = 410 (0.5, M^+), 341 [26, M^+–H_2C=$CHC(CH_3)_2$], 309 [100, M^+–$H_3COC(C_2H_5)_2$]. - $C_{23}H_{46}N_2O_2Si$ (410.7): calcd. C 67.26, H 11.29, N 6.82; found C 67.22, H 11.50, N 7.18.

(2S,2'R,3'S)-1-(2'-tert-Butyldimethylsilyloxy-3'-ethyl-1'-pent-4'-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R,S*)-**9c**]: 92% Yield from hydrazone **8c** after column chromatography (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - $[\alpha]_D^{RT}$: +49.3 (c = 1.2, $CHCl_3$), After HPLC (diethyl ether/ light petroleum, 3:97, flow: 18 ml/ min, R_t = 22.6 min). - R_f = 0.30 (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - *syn* = 92% (93% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 92% (> 98% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 1640 (w, C=C), 1600 (m, C=N), 1070 (s, SiOC) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.01, 0.06 [s, 6H, $Si(CH_3)_2$], 0.83-0.87 [m, 18H, 9 ($C(CH_3)_3$, 3 $CHCH_2CH_3$, 6 $C(CH_2CH_3)_2$], 1.20-2.05 [m, 10H, 4 ring-CH_2, 2 $CHCH_2CH_3$, 4 $C(CH_2CH_3)_2$], 2.15 (m, 1H, $CHCH_2CH_3$), 2.73 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH_3), 3.27 (m, 1H, HC*H*N), 3.55 (dd, *J* = 8.7 Hz/ 3.0 Hz, 1H, CHN), 4.07 (t, *J* = 6.7 Hz, 1H, CHOSi), 4.97 (ddd, *J* = 17.1 Hz/ 2.3 Hz/ 1.7 Hz, 1H, HC=CCHH_{cis}), 5.02 (dd, *J* = 10.1 Hz/ 2.3 Hz, 1H, HC=CCHH_{trans}), 5.62 (ddd, *J* = 17.1 Hz/ 10.4 Hz/ 8.7 Hz, 1H, *H*C=CH_2), 6.31 (d, *J* = 6.8 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = –4.72, –3.76, 7.80, 8.56, 11.66, 18.25, 22.71, 23.69, 23.76, 24.63, 26.26, 25.96, 50.38, 50.67, 52.17, 68.43, 76.28, 80.41, 115.90, 136.28, 139.28 ppm. - GC/MS (70 eV): *m/z* (%) = 309 [100, M^+–$H_3COC(C_2H_5)_2$], 70 (14, $C_4H_8N^+$). - $C_{23}H_{46}N_2O_2Si$ (410.7): calcd. C 67.26, H 11.29, N 6.82; found C 66.89, H 11.38, N 6.82.

(2S,2'R,3'S)-1-(2'-tert-Butyldimethylsilyloxy-3'-propyl-1'-pent-4'-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R,S*)-**9d**]: 93% Yield from hydrazone **8d** after column chromatography (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - $[\alpha]_D^{RT}$: +46.0 (c = 1.1, $CHCl_3$), After HPLC (diethyl ether/ light petroleum, 4:96, flow: 18 ml/ min, R_t = 14.3 min). - R_f = 0.31 (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - *syn* = 92% (93% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 92% (> 98% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 1640 (w, C=C), 1600 (m, C=N), 1070 (s, SiOC) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.01, 0.06 [s, 6H, $Si(CH_3)_2$], 0.83-0.92 [m, 18H, 9 ($C(CH_3)_3$, 3

$CH_2CH_2CH_3$, 6 $C(CH_2CH_3)_2$], 1.20-2.05 [m, 12H, 4 ring-CH_2, 4 $CH_2CH_2CH_3$, 4 $C(CH_2CH_3)_2$], 2.25 (m, 1H, $CHCH_2CH_2$), 2.74 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH_3), 3.27 (m, 1H, HC*H*N), 3.54 (dd, J = 8.7 Hz/ 3.0 Hz, 1H, CHN), 4.07 (t, J = 6.7 Hz, 1H, CHOSi), 4.94 (m, 2H, HC=CH_2), 5.65 (ddd, J = 17.1 Hz/ 10.4 Hz/ 8.7 Hz, 1H, *H*C=CH_2), 6.31 (d, J = 6.7 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = –4.72, –3.80, 7.80, 8.56, 14.23, 18.25, 20.22, 23.71, 23.77, 24.62, 26.24, 25.97 , 32.14, 50.19, 50.39, 50.70, 68.45, 76.42, 80.41, 115.62, 136.31, 139.59 ppm. - MS (70 eV) m/z (%) = 323 [100, M^+–$H_3COC(C_2H_5)_2$], 70 (12, $C_4H_8N^+$). - $C_{24}H_{48}N_2O_2Si$ (424.7): calcd. C 67.87, H 11.39, N 6.60; found C 68.00, H 11.63, N 6.64.

(2S,2´R,3´S)-1-(2´-tert-Butyldimethylsilyloxy-3´-isopropyl-1´-pent-4´-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R,S*)-**9e**]: 96% Yield from hydrazone **8e** after column chromatography (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - $[\alpha]_D^{RT}$: +67.6 (c = 1.0, $CHCl_3$), After HPLC (diethyl ether/ light petroleum, 4:96, flow: 18 ml/ min, R_t = 19.4 min). - R_f = 0.31 (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - *syn* = 87% (90% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 91% (> 98% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 1640 (w, C=C), 1600 (m, C=N), 1070 (s, SiOC) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.01, 0.07 [s, 6H, $Si(CH_3)_2$], 0.82-0.93 [m, 21H, 9 ($C(CH_3)_3$, 6 $CH(CH_3)_2$, 6 $C(CH_2CH_3)_2$], 1.40-2.10 [m, 10H, 4 ring-CH_2, $CHCH(CH_3)_2$, 4 $C(CH_2CH_3)_2$], 2.75 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH_3), 3.27 (m, 1H, HC*H*N), 3.54 (dd, J = 8.8 Hz/ 3.0 Hz, 1H, CHN), 4.18 (t, J = 7.4 Hz, 1H, CHOSi), 4.93 (ddd, J = 17.4 Hz/ 2.3 Hz/ 0.7 Hz, 1H, HC=CHH_{cis}), 5.04 (dd, J = 10.1 Hz/ 2.7 Hz, 1H, HC=CHH_{trans}), 5.52 (ddd, J = 17.1 Hz/ 10.4 Hz/ 9.7 Hz, 1H, *H*C=CH_2), 6.27 (d, J = 7.1 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = –4.76, –3.53, 7.78, 8.56, 17.82, 21.48, 18.22, 23.65, 23.77, 24.66, 26.26, 25.98, 26.66, 50.38, 50.63, 56.69, 68.38, 74.37, 80.40, 117.42, 136.23, 136.68 ppm. - MS (70 eV): m/z (%) = 341 [11, M^+–H_2C=CHCH(*i*-Pr)], 323 [100, M^+–$H_3COC(C_2H_5)_2$]. - $C_{24}H_{48}N_2O_2Si$ (424.7): calcd. C 67.87, H 11.39, N 6.60; found C 68.15, H 11.25, N 6.81.

(2S,2´R,3´S)-1-(3´-Butyl-2´-tert-butyldimethylsilyloxy-1´-pent-4´-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R,S*)-**9f**]: 91% Yield from hydrazone **8f** after column chromatography (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - $[\alpha]_D^{RT}$: +46.9 (c = 1.0, $CHCl_3$), After HPLC (diethyl ether/ light petroleum, 3:97, flow: 18 ml/ min, R_t = 18.6 min). - R_f = 0.35 (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - *syn* = 90% (96% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 91% (> 98% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 1640 (w, C=C), 1600 (m, C=N), 1070 (s, SiOC) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.01, 0.06 [s, 6H, $Si(CH_3)_2$], 0.83-0.92 [m, 18H, 9 ($C(CH_3)_3$, 3 $CH_2CH_2CH_3$, 6 $C(CH_2CH_3)_2$], 1.15-2.05 [m, 14H, 4 ring-CH_2, 6 $CH_2CH_2CH_2CH_3$, 4 $C(CH_2CH_3)_2$], 2.74 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH_3), 3.27 (m, 1H, HC*H*N), 3.53 (dd, J = 9.1 Hz/ 3.4 Hz, 1H, CHN), 4.06 (t, J = 6.3 Hz, 1H, CHOSi), 4.99 (m, 2H, HC=CH_2), 5.65 (ddd, J = 17.1 Hz/ 10.4 Hz/ 8.7 Hz, 1H, *H*C=CH_2), 6.31 (d, J = 6.7 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = –4.72, –3.80, 7.79, 8.56, 14.06, 18.25, 22.90, 23.69, 23.76, 24.61, 26.23, 25.96, 29.35, 29.61, 50.39, 50.41, 50.70, 68.44, 76.45, 80.41, 115.66, 136.31, 139.63 ppm. - MS (70 eV): m/z (%) = 341 [14, M^+-H_2C=CHCH(*n*-Bu)], 337 [100, M^+-$H_3COC(C_2H_5)_2$], 73 (100). - HRMS: calcd. for [M^+-$H_3COC(C_2H_5)_2$] $C_{19}H_{37}N_2OSi$ 337.2675; found 337.2677.

(2S,2´R,3´S)-1-(2´-tert-Butyldimethylsilyloxy-3´-isobutyl-1´-pent-4´-enylidenamino)-2-(1-ethyl-1-methoxypropyl)-pyrrolidine [(*S,R,S*)-**9g**]: 74% Yield from hydrazone **8g** after column chromatography (diethyl ether/ light petroleum, 1:20, 2.5% NEt_3). - $[\alpha]_D^{RT}$: +56.5 (c = 1.0, $CHCl_3$), After HPLC (diethyl ether/ light petroleum, 2.5:97.5, flow: 18 ml/ min, R_t = 21.1 mi.). - R_f = 0.87 (diethyl ether/ light petroleum, 1:2). - *syn* = 88% (98% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - *de* = 90% (> 98% After HPLC), determined by ^{13}C NMR (2 h, 300 MHz). - IR (film): ν = 1640 (w, C=C), 1600 (m, C=N), 1070 (s, SiOC) cm^{-1}. - ^1H NMR (300 MHz): δ = 0.01, 0.06 [s, 6H, $Si(CH_3)_2$], 0.82-0.92 [m, 21H, 9 ($C(CH_3)_3$, 6 $CH(CH_3)_2$, 6 $C(CH_2CH_3)_2$], 1.15-2.05 [m, 11H, 4 ring-CH_2, 3 $CH_2CH(CH_3)_2$, 4 $C(CH_2CH_3)_2$], 2.34 (m, 1H, $CHHC{=}CH_2$), 2.74 (m, 1H, *H*CHN), 3.23 (s, 3H, OCH_3), 3.27 (m, 1H, HC*H*N), 3.54 (dd, *J* = 8.7 Hz/ 3.4 Hz, 1H, CHN), 4.04 (t, *J* = 6.4 Hz, 1H, CHOSi), 4.99 (m, 2H, $HC{=}CH_2$), 5.64 (ddd, *J* = 16.8 Hz/ 10.4 Hz/ 8.7 Hz, 1H, $HC{=}CH_2$), 6.32 (d, *J* = 6.7 Hz, 1H, HC=N) ppm. - ^{13}C NMR (75 MHz): δ = –4.71, –3.82, 7.80, 8.54, 18.25, 21.76, 23.70, 25.06, 23.733, 23.77, 24.62, 26.23, 25.96, 39.20, 48.40, 50.39, 50.73, 68.48, 76.61, 80.42, 115.54, 136.36, 139.08 ppm. - MS (70 eV): *m/z* (%) = 341 [15, $M^+–H_2C{=}CHCH(i\text{-}Bu)$], 337 [100, $M^+–H_3COC(C_2H_5)_2$]. - $C_{25}H_{50}N_2O_2Si$ (438.8): calcd. C 68.44, H 11.49; N 6.39; found C 68.62, H 11.35, N 6.89.

(2S,3R,4R)-4-tert-Butyldimethylsilyloxy-2-iodomethy-3-methyl-tetrahydrofuran [2,3-*cis*-3,4-*trans*-**12**]: Aldehyde **11a** (0.30 mmol) was reduced with $NaBH_4$ according to standard procedure and cyclised with I_2 according to literature[22]. Purification by column chromatography (diethyl ether/ light petroleum, 1:20) yielded the pure tetrahydrofuran (77% from aldehyde **11a**) as a colourless liquid. - R_f = 0.76 (diethyl ether/ light petroleum, 1:2). - 2,3-*cis*/ 2,3-*anti* = 73/ 27, Determined by GC (OV-1-CB, 80-10-300, R_t = 9.9 min, 10.2 min). - (IR (film): ν = 1110 (s, COC), 1080 (s, SiOC), 840 (s, CSi-O), 780 (OSi-C) cm^{-1}. - ^1H NMR (500 MHz): δ = 0.05, 0.07 [s, 6H, $Si(CH_3)_2$], 0.85 (d, *J* = 7.3 Hz, 3H, $CHCH_3$), 0.89 [s, 9H, $C(CH_3)_3$], 2.21 (qdd, *J* = 7.3 Hz/ 4.8 Hz/ 1.6 Hz, 1H, $CHCH_3$), 3.07 (dd, *J* = 9.8 Hz/ 7.8 Hz, 1H, *H*CHI), 3.24 (dd, *J* = 9.8 Hz/ 6.9 Hz, 1H, HC*H*I), 3.70 (dd, *J* = 9.1 Hz/ 1.6 Hz, 1H, *H*CHO), 4.09 (dt, *J* = 4.5 Hz/ 1.5 Hz, 1H, CHOSi), 4.12 (dd, *J* = 9.1 Hz/ 4.5 Hz, 1H, HC*H*O), 4.38 (td, *J* = 7.3 Hz/ 4.8 Hz, 1H, $CHCH_2I$) ppm. - ^{13}C NMR (125 MHz): δ = –4.81, –4.71, 3.43, 10.65, 18.03, 25.78, 44.93, 75.40, 79.29, 80.41 ppm. - GC/MS (70 eV): *m/z* (%) = 299 [1.6, $M^+–C(CH_3)_3$], 117 (100). - $C_{12}H_{25}IO_2Si$ (356.3): calcd. C 40.45, H 7.07; found C 40.46, H 7.18.

(3´R,4´R,5´S,R-)- and (3´R,4´R,5´S,S-)-Methoxy-phenyl-acetic acid (5-iodomethyl-4-methyl-tetrahydrofuran-3-yl) ester [(*R*)-**13**, (*S*)-**13**]: Tetrahydrofuran **11** (0.15 mmol) was desilylated by stirring in 3% methanolic HCl (5 ml) until complete conversion (TLC control). The solution was transferred to a separating funnel, diluted with water and extracted with CH_2CH_2 (3 x 20 ml). The organic phase was dried over $MgSO_4$ and evaporated. The crude alcohol was converted to the (*R*)- and (*S*)-MPA ester according to literature procedure[16]. Purification by column chromatography (diethyl ether/ light petroleum, 1:4) yielded the pure esters (76% from terahydrofuran **12**) as colourless liquids. - R_f = 0.30 (diethyl ether/ light petroleum, 1:2). - (IR (film): ν = 1750 (s, C=O), 1110 (s, COC) cm^{-1}. - ^1H NMR (500 MHz): (*R*)-**13**: δ = 0.93 (d, *J* = 7.4 Hz, 3H, $CHCH_3$), 2.47 (qdd, *J* = 7.1 Hz/ 4.6 Hz/ 0.5 Hz, 1H, $CHCH_3$), 3.02 (dd, *J* = 9.9 Hz/ 8.4 Hz, 1H, *H*CHI), 3.23 (ddt, *J* = 9.8 Hz/ 6.5 Hz/ 0.5 Hz, 1H, HC*H*I), 3.41 (s, 3H, OCH_3), 3.62 (dd, *J* = 10.8 Hz/ 1.6 Hz, 1H, *H*CHO), 4.18 (ddd, *J* = 10.8 Hz/ 4.9 Hz/ 0.5 Hz, 1H, HC*H*O), 4.23 (ddd, *J* = 8.3 Hz/ 6.5 Hz/ 4.6 Hz, 1H,

C$H$$CH_2$I), 4.78 (s, 1H, *C*HOCH$_3$), 5.05 (m, 1H, CHOCO), 7.32-7.47 (m, 5H, CH_{arom}) ppm; (*S*)-**13**: δ = 0.87 (d, *J* = 7.4 Hz, 3H, CHC*H*$_3$), 2.17 (m, 1H, C*H*CH$_3$), 2.96 (dd, *J* = 9.9 Hz/ 8.2 Hz, 1H, *H*CHI), 3.19 (ddt, *J* = 9.8 Hz/ 6.6 Hz/ 0.5 Hz, 1H, HC*H*I), 3.42 (s, 3H, OCH$_3$), 3.85 (ddd, *J* = 10.8 Hz/ 1.5 Hz/ 0.5 Hz, 1H, *H*CHO), 4.07 (dddd, *J* = 8.1 Hz/ 6.6 Hz/ 4.6 Hz/ 0.4 Hz, 1H, C*H*CH$_2$I), 4.24 (ddd, *J* = 10.8 Hz/ 4.7 Hz/ 0.5 Hz, 1H, HC*H*O), 4.77 (s, 1H, C*H*OCH$_3$), 5.05 (m, 1H, CHOCO), 7.33-7.46 (m, 5H, CH_{arom}) ppm. - ^{13}C NMR (125 MHz) [(*R*)-**13**]: δ = 1.79, 10.21, 41.85, 57.36, 72.11, 80.75, 81.51, 82.51, 127.14, 128.82, 128.99, 135.84, 170.28 ppm. - GC/MS (70 eV): *m/z* (%) = 390 (1.2, M^+), 121 (100, $C_6H_5CHOCH_3^+$). - $C_{15}H_{19}IO_4$ (390.2): calcd. C 46.17, H 4.91; found C 46.13, H 4.97.

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