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Preparation of 1,2 Aminols from Cyanohydrins *via* *N*-Diisobutylaluminium Imines.

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Abstract : The *N*-Aluminium imines derived from cyanohydrins have been used in the synthesis of α-amino alcohols with high diastereoselectivity.

Introduction

The development of efficient and highly selective methods for carbon-carbon bond formation has been and continues to be a challenging and exciting endeavour in organic chemistry. Especially in the field of asymmetric synthesis the chemical community has seen a real breakthrough in the past several years and different processes routinely allowing asymmetric induction of greater then 90% diastereomeric or/and enantiomeric excess are now at our disposal.[1] In recent years we have developed a general method for the asymmetric C-C bond formation α to an amino group *via* chiral metallo-imines[2].

N - Metallo imines can be regarded as masked imine derivatives of ammonia. They have been used in the preparation of primary amines[3], β-lactams[4], in the synthesis of secondary carbinamines[5], aziridines[6], pyrrolines and piperidines[7], 1,2-diamines[8] and optically active secondary carbinamines[9]. Chiral *N*-trimethylsilyl imines, derived from mandelic or lactic aldehydes have been used in a high stereocontrolled total synthesis of carbapenem (+) PS-5[10], (+) PS-6[11] and monobactam Aztreonam[12].

In a recent letter[13] we briefly described a novel synthesis of *N*-unsubstituted aminols starting from nitriles *via* *N*-aluminium imines. Chiral α-amino alcohols[14] not only occur as natural products[15] and drugs[16] but are also components of amino sugars[17] and of certain peptides and peptide analogues[18]. Our novel reaction takes place by the addition of diisobutylaluminium hydride (DIBAH)[19] to *O*-protected cyanohydrin followed by treatment of the *N*-aluminium imine thus obtained with C-nucleophiles (Scheme 1). In this paper we report the results of a detailed study of this reaction on a range of cyanohydrins.

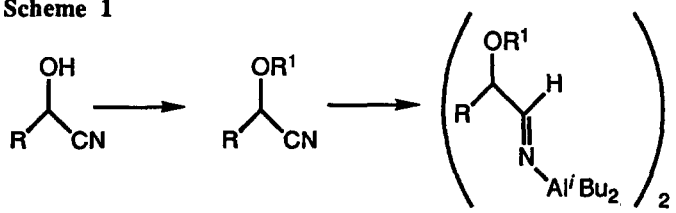
Results and discussion

The starting point in the synthesis of α-amino alcohols was the preparation of *N*- diisobutylaluminium imines. These imines were generated by treatment of a solution of cyanohydrin **2** in pentane with diisobutylaluminium hydride DIBAH (1.1 eq) at -78°C (Scheme 1)

Infrared spectra (in pentane) of the colourless solution of the crude mixture obtained from the reaction of *O*-silyl protected mandelonitrile **2a**, chosen as the representative example, and DIBAH, shows an adsorption at 1670 cm^{-1} assigned to C=N stretching. The analysis of the ^1H N.M.R. 300 MHz spectrum of **3a** (Toluene-d_8)

shows two doublets of the same intensity at 8.26 (J= 3 Hz) and 8.27 (J= 3 Hz), and two doublets, once again with the same intensity, at 8.31 (J= 3 Hz) and 8.33 (J= 3 Hz).

Scheme 1

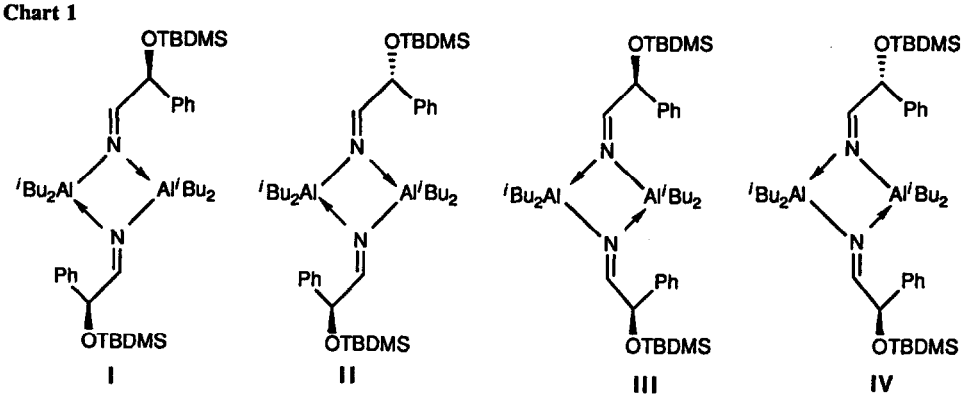


1 **2** **3**

1a, 2a, 3a: R=Phenyl, R^1=TBDMS; **1b, 2b, 3b:** R=Phenyl, R^1=Me; **1i, 2i, 3i:** R=Methyl, R^1=TBDMS; **1j, 2j, 3j:** R=Methyl, R^1=Trityl; **1o, 2o, 3o:** R=Octyl, R^1=TBDMS; **1p, 2p, 3p:** R=Propen-1-yl, R^1=TBDMS.

The intensity ratio of the first set of signals against the second is 75/25. The first two doublets have been assigned to the diastereomeric "*trans* " dimers **I** and **II** (For the sake of simplicity only one enantiomer has been reported) and the second one attributed to the "*cis* " dimers **III** and **IV** (Chart 1)[20]. All these compounds arise from the dimerization of (*R,S*)-2-[(*tert* -butyldimethylsilyl)oxy]-2-phenyl-*N*-(diisobutylaluminium)ethanimine **3a**. These two sets of signals progressively broaden and submerge each other taking the ^{1}H NMR at a range of temperatures between +20°C and +100°C. This fact suggests the existence of an equilibrium between the couple of dimers **I, II** and **III, IV** respectively. Work is in progress on this topic and will be published on due course.

Chart 1



Reaction of the mixture of dimers **3a** with allylmagnesium chloride (4 eq) furnishes the corresponding α-amino alcohols **4a** and **5a** (Scheme 2). Following this procedure a number of α-amino alcohols have been prepared, the results being reported in Table 1 with the relative diastereomeric ratio.

Although the yields of the reaction are not excellent, it must be pointed out that the reaction is a one pot-two steps type reaction. Moreover the work-up of the crude reaction mixture, after the addition of DIBAH, gives rise to the mandelaldehyde in 65% yield. The low yields obtained may be partially ascribed to a competitive cleavage of the *tert* -butyldimethylsilyl group by means of DIBAH, as recently reported[21]. The use of *tert*-butylmethyl ether as the solvent, known to lower this side reaction[22], results in an increase of the reaction yield but, at the same time, in the lowering of the diastereomeric ratio (see Exps 3 and 5 Table 1). Moreover substitution of the *tert* -butyldimethylsilyl group with the methyl or trityl one doesn't cause a substantial increase

in yield. However the *O*-protection is crucial for the success of the reaction since treatment of the unprotected cyanohydrins with DIBAH gives rise to an alcoholate which spontaneously eliminates CN^-, affording the corresponding aldehyde, even at low temperature.

Lithium alkyls and allyl magnesium chloride have been used as nucleophiles. Other Grignard reagents seem to fail in giving the expected aminols. This failure has been ascribed to a higher basicity of Grignard reagents compared to lithium ones[23], so that an α-deprotonation takes place and a complex mixture of products results from the reaction.

The reaction requires four equivalents of nucleophile to one mole of dimer to give better yields. Upon treatment of the dimer with two equivalents of nucleophile, the dimer itself collapses to the corresponding "*ate*" complex "**A**" which in turn adds another equivalent of the nucleophile to give the end product (Scheme 2).

Scheme 2

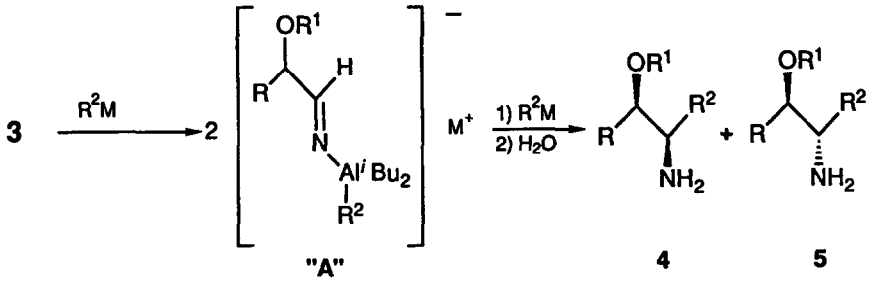


Table 1 1,2-Aminols from Cyanohydrins[24].

Exp	R	R^1	R^2-M	Products	*Syn / Anti*	Yields %
1	Phenyl	TBDMS	AllylLi	**4a : 5a**	91/9	43
2	Phenyl	TBDMS	AllylMgCl	**4a : 5a**	86/14	26
3	Phenyl	TBDMS	AllylMgCl	**4a : 5a**	70/30	48[a]
4	Phenyl	Me	AllylMgCl	**4b : 5b**	71/29	30
5	Phenyl	Me	AllylMgCl	**4b : 5b**	67/33	56[a]
6	Phenyl	TBDMS	MethylLi	**4c : 5c**	75/25	29
7	Phenyl	TBDMS	*n* - ButylLi	**4d : 5d**	91/9	48
8	Phenyl	TBDMS	*s*- ButylLi	**4e : 5e**	67/33	45[b]
9	Phenyl	TBDMS	*t* - ButylLi	**4f : 5f**	12/88	27
10	Phenyl	TBDMS	*n* - PentylLi	**4g : 5g**	87/13	40
11	Phenyl	TBDMS	*n* - HexylLi	**4h : 5h**	81/19	35
12	Methyl	TBDMS	*n* - ButylLi	**4i : 5i**	76/24	57
13	Methyl	Trityl	*n* - ButylLi	**4j : 5j**	85/15	70
14	Methyl	TBDMS	*t* -ButylLi	**4k : 5k**	45/55	60
15	Methyl	TBDMS	CyclopropylLi	**4l : 5l**	86/14	40
16	Methyl	TBDMS	AllylLi	**4m : 5m**	71/29	47
17	Methyl	TBDMS	AllylMgCl	**4m : 5m**	65/35	44
18	Methyl	Trityl	AllylMgCl	**4n : 5n**	65/35	56
19	Octyl	TBDMS	AllylMgCl	**4o : 5o**	51/49	50
20	Propen-1-yl	TBDMS	*n* - ButylLi	**4p : 5p**	90/10	30
21	Propen-1-yl	TBDMS	*i* - ButylLi	**4q : 5q**	88/12	36
22	Propen-1-yl	TBDMS	AllylMgCl	**4r : 5r**	77/23	30

a) Reaction performed in *tert* - butylmethyl ether. b) See note [25].

One interesting feature of the reaction documented in Table 1 is the *syn* diastereoselectivity, the diastereomeric ratio being calculated on the crude reaction mixture. The stereochemical assignments of *O*-protected alcohols **4** and **5**, have been attributed on the basis of the ^1H and ^{13}C N.M.R. spectra of the corresponding 1,3-oxazolidin-2-ones. For this purpose, compounds **4** and **5** protected as *tert*-butyldimethylsilyl ether[26], were reacted with di-*tert*-butyl carbonate, in dioxane in basic medium (aqueous NaOH), to give the *tert*- Boc derivatives **6** and **7**. After desilylation with tetrabutylammonium fluoride, the corresponding alcohols **8** and **9** were cyclized to oxazolidinones **10** and **11** by treatment with NaH in N,N-dimethylformamide. Flash chromatography of the crude reaction mixture allowed the separation of diastereoisomers in most cases (Scheme 3).

Scheme 3

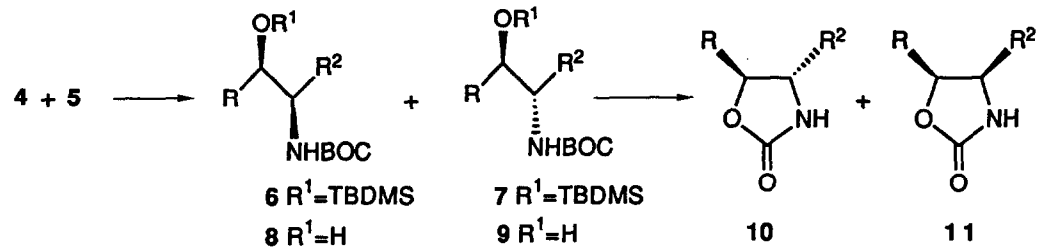


Table 2: Chemical Shifts and Coupling Constants for ^1H NMR of the Oxazolidin-2-one Derivatives **10** and **11**.

R	R^2	Prod	δ H(4)	δH(5)	J4-5	Prod	δ H(4)	δ H(5)	J4-5
Phenyl	Allyl	**10a**	3.80	5.18	6.0	**11a**	4.07	5.77	8.0
Phenyl	*n* - Butyl	**10b**	3.74	5.13	6.4	**11b**	4.03	5.71	8.1
Phenyl	*s* - Butyl	**10c***	3.64 (3.67)	5.23 (5.24)	4.8 (5.2)	**11c***	3.93 (4.00)	5.65 (5.72)	8.1 (8.4)
Phenyl	*t* - Butyl	**10d**	3.45	5.28	3.8	**11d**	3.85	5.73	7.7
Phenyl	*n* - Pentyl	**10e**	3.72	5.11	6.5	**11e**	4.03	5.71	8.2
Phenyl	Methyl	**10f**	3.84	5.03	7.4	**11f**	4.21	5.71	8.0
Methyl	Allyl	**10g**	3.48	4.35	6.1	**11g**	3.83	4.82	7.4
Methyl	*n* - Butyl	**10h**	3.39	4.28	6.3	**11h**	3.75	4.76	7.0
Methyl	*t* -Butyl	**10i**	3.09	4.46	4.6	**11i**	3.50	4.79	7.0
Methyl	Cycloprop	**10j**	2.79	4.49	6.3	**11j**	3.03	4.79	7.9
Propen-1-yl	Allyl	**10k**	3.58	4.56	7.0	**11k**	3.83	5.04	7.9
Propen-1-yl	*iso* - Butyl	**10l**	3.57	4.46	7.4	**11l**	3.90	4.99	8.2

*: Due to the presence of an extra stereogenic center (C-3) the values for the other couple of isomers are reported in brackets; See note 26.

There are unequivocal differences between the spectra of the two oxazolidin-2-ones. The ^1H NMR spectra of **10** and **11**, although generally similar, are clearly different in the H(4) and H(5) chemical shift and coupling constant (J) between the two annular protons. Both spectra are characterised by two multiplets with different coupling constants and different chemical shifts.

It is known[27] that the *trans* 1,3-oxazolidin-2-one, generated from the *syn* isomer of the acyclic amino alcohol, shows a coupling constant generally *smaller* than the *cis* oxazolidin-2-ones (4-6 Hz against 6-9 Hz) generated from the *anti* amino alcohol. From the analysis of the H(4)-H(5) coupling constants, it has then been

possible to attribute the correct stereochemistry to both isomers. Furthermore the two side chains directly linked to the carbon atoms C(4) and C(5) cause a deshielding effect on the annular protons. This effect is particularly large when the stereorelationship of the two protons is *trans* . In this case, in fact, the two protons and the two side chains eclipse each other (See Table 2). A final proof of the correct attribution comes from the ^{13}C-N.M.R. spectra analysis. It is indeed known that the ^{13}C chemical shift in the isomer with *cis* connection is generally more shielded than with the *trans* one by steric compression. (see Table 3).

Table 3: Chemical Shifts at ^{13}C NMR for the Oxazolidin-2-one Derivatives **10** and **11.**

R	R^2	Product	δ C(4)	δ C(5)	Product	δ C(4)	δ C(5)
Phenyl	Allyl	**10a**	39.0	138.5	**11a**	36.1	134.9
Phenyl	*n* - Butyl	**10b**	34.5	138.6	**11b**	31.4	135.2
Phenyl	*sec* - Butyl	**10c***	38.8 (39.1)	139.4 (139.5)	**11c***	34.8 (34.5)	135.1 (135.2)
Phenyl	*t* - Butyl	**10d**	34.1	140.1	**11d**	34.0	135.3
Phenyl	*n* - Pentyl	**10e**	34.9	138.4	**11e**	31.3	135.1
Phenyl	Methyl	**10f**	19.7	137.9	**11f**	19.5	135.1
Methyl	Allyl	**10g**	38.5	19.6	**11g**	34.0	14.2
Methyl	*n* - Butyl	**10h**	34.4	20.0	**11h**	29.3	14.5
Methyl	*t* -Butyl	**10i**	33.2	22.0	**11i**	33.5	16.3
Methyl	Cycloprop	**10j**	14.3	20.2	**11j**	10.8	15.5
Propen-1-yl	Allyl	**10k**	38.5	127.1	**11k**	35.7	123.7
Propen-1-yl	*iso* - Butyl	**10l**	43.5	127.3	**11l**	39.6	124.1

*: Due to the presence of an extra stereogenic center (C-3) the values for the other couple of isomers are reported in brackets; See note 26.

The addition of Lewis acids to the dimeric aluminium imines does not show any effect on the reaction yield but, instead, lowers the stereoselectivity of the reaction (see Table 4 where allyl magnesium chloride and aluminum imines arising from lactic and mandelic nitriles were chosen as representative substrates).

Table 4 1,2-Aminols from Cyanohydrins in the presence of Lewis acids.

Exp	R	R^1	R^2	Lewis acid	Products	*Syn / Anti*	Yields %
1	Phenyl	TBDMS	AllylMgCl	$CeCl_3$	**4a : 5a**	83/17	36
2	Phenyl	TBDMS	AllylMgCl	MgI_2	**4a : 5a**	75/25	30
3	Phenyl	TBDMS	AllylMgCl	$ZnBr_2$	**4a : 5a**	60/40	40
4	Phenyl	TBDMS	AllylMgCl	BF_3 Et_2O	**4a : 5a**	50/50	51
5	Phenyl	TBDMS	AllylMgCl	CuI/BF_3 Et_2O	**4a : 5a**	66/34	41
6	Methyl	TBDMS	AllylMgCl	$ZnBr_2$	**4m : 5m**	60/40	43
7	Methyl	TBDMS	AllylMgCl	CuI/BF_3 Et_2O	**4m : 5m**	66/34	30
8	Methyl	Trityl	AllylMgCl	BF_3 Et_2O	**4n : 5n**	50/50	60
9	Phenyl	Me	AllylMgCl	BF_3 Et_2O	**4b : 5b**	50/50	10
10	Phenyl	Me	AllylMgCl	Et_2AlCl	**4b : 5b**	58/42	16

As reported above the reaction shows a high *syn* diastereoselectivity. However, on going from the primary, secondary and tertiary lithium alkyls a remarkable increase of the *anti* diastereoselectivity is observed (see Expts 7, 8, 9 Table 1). This stereochemical behaviour can be explained, at least in part, by assuming a

coplanarity between the oxygen and the nitrogen atoms in the imine due to the chelation of the metal of the nucleophile[28] (Fig. 1). Using this chelated model, the R and the silyloxy group are lying as far apart from each other as possible in order to minimise the non bonded interactions. The approaching nucleophile will therefore experience two different and opposite repulsive interactions: a 1,2 interaction with the R group and a 1,3 interaction with the bulky silyloxy group. If the nucleophile is small, the *n*- butyl group for instance, the 1,2 repulsive interaction with the R group of the imine is the most important so that the attack occurs from the opposite side of the R group leading to the *syn* isomer (*Path A* Fig 1). On the contrary, when the nucleophile is a large one, as in the case of the *tert*-butyl group, the 1,3 interaction with the silyloxy group becomes important and controls the addition forcing the nucleophile to attack from the same side of the R group thus giving rise to the formation of the *anti* isomer (*Path B* Fig 1).

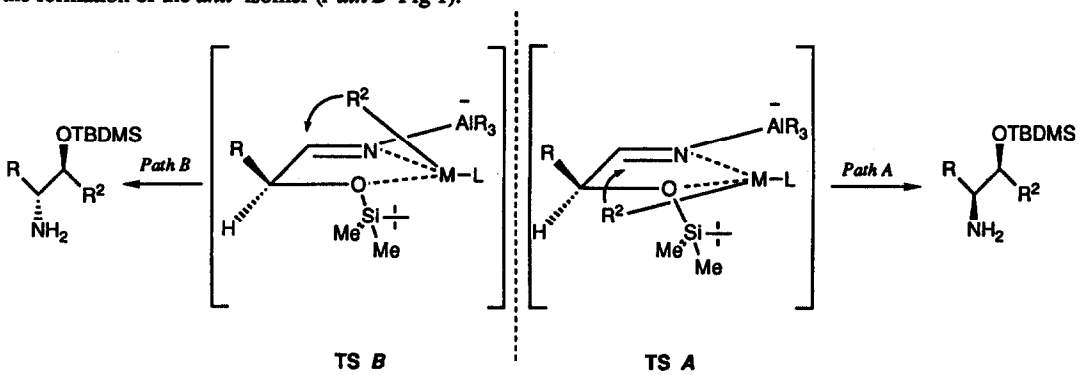


Fig. 1

In conclusion, the reaction of the α-hydroxy aluminium imines with a C-nucleophile provides a satisfactory method of preparation with a high degree of diastereoselectivity α-amino alcohols from cyanohydrins.

EXPERIMENTAL

General. For purification of crude reaction mixtures, flash chromatography using silica gel 70-230 mesh was used in most cases. Analytical thin layer chromatography was performed by using precoated silica gel F-254 plates; products were observed by using ultraviolet light, iodine or phosphomolybdate spot tests.
Materials. The solvents used were predried according literature procedures. ^{1}H- and ^{13}C-NMR data were obtained as $CDCl_3$ solution on 90 and 300 MHz spectrophotometer, chemical shifts are reported in parts per million (ppm) and coupling constants in Hz. Infrared spectra were obtained as liquid films or in nujol dispersions and frequencies are reported in cm^{-1}. Mass spectra were recorded at an ionisation energy of 70 eV. Exact mass were recorded at mass spectrophotometer VG 7070 E.

Preparation of (*R,S*)-phenyl-(*t*-butyl)-dimethylsilyloxy-ethanenitrile 2a.

To a stirred solution of (*R,S*)-mandelonitrile (100 mmol, 13.3 g) in *N,N*-dimethylformamide (50 ml) was added imidazole (200 mmol, 13.6 g) and *t* -butyldimethylsilyl chloride (TBDMSCl) (110 mmol 16.4 g) at room temperature under argon atmosphere. The mixture was stirred overnight. After addition of aqueous 3N HCl (70 ml) and ice (20 g), extraction with ether, drying (anhydrous $MgSO_4$), and evaporation of solvent, the residue was purified by distillation in vacuum (157°C at 18 mmHg) affording compound **2a** (19.8 g) in 80% yield.

(M^+-15, *Calcd* for $C_{13}H_{18}NOSi$: 232.1157 *Found* 232.1154), *m/e* 232 (M^+-CH_3), 190 , 116, 104, 84. IR (film): 3060, 3020, 2960-2860, 1490, 1470, 1450. ^{1}H-NMR (90 MHz) 0.17 (s, 3 H), 0.23 (s, 3 H), 0.97 (s, 9 H), 5.50 (s, 1 H), 7.20-7.50 (m, 5 H)

Preparation of (*R,S*)-2-methoxy-2-phenyl-ethanenitrile 2b

In a two-necked round bottom flask $CoCl_2$ (0.4 mmol, 0.1 g) and TMSCN (30 mmol, 4 ml) were suspended in dry dichloromethane (150 ml) under argon atmosphere and the mixture was stirred for 30 minutes at room temperature. To this suspension a solution of α,α-dimethoxy-toluene (20 mmol, 3 ml) in CH_2Cl_2 (50 ml) was added dropwise at the same temperature and the reaction stirred for three hours. After treatment with phosphate buffer, extraction with dichloromethane, drying over magnesium sulfate, concentration in vacuo, the crude was successively bulb to bulb distilled to give the expected product in 70% yield.
(M^+, *Calcd* for C_9H_9NO: 147.0684 *Found* 147.0688), *m/e* 147 (M^+), 132, 116 (base-peak), 105, 89, 77. IR (film): 3060, 3030, 3000, 2930, 2820, 1490, 1450, 1450, 1200. ^{1}H-NMR (90 MHz) 3.50 (s, 3 H), 5.12 (s, 1 H), 7.30-7.55 (m, 5 H)

Preparation of (*R,S*)-2-(*t*-butyl)dimethylsilyloxy-propionitrile 2i.

This compound was obtained following the procedure reported for **2a** starting from (*R,S*)-lactonitrile (138 mmol, 9.8 g) .Distillation in vacuum (80°C at 18 mmHg) afforded **2i** (25.5 g) in 70% yield.
(M^+, *Calcd* for $C_9H_{19}NOSi$: 185.1236 *Found* 185.1239), *m/e* 185 (M^+), 120, 101, 84, 73, 45. IR: (film) 2960-2860, 2250, 1490, 1470, 1450. ^{1}H-NMR (90 MHz) 0.20 (s, 3 H), 0.25 (s, 3 H), 0.99 (s, 9 H), 1.60 (d, 3 H J=6.0), 4.60 (q, 1 H J=6.0)

Preparation of (*R,S*)- 2-triphenylmethoxy-propionitrile 2j.

To a solution of (*R,S*)-lactonitrile (3.6 g, 50 mmol) in *N,N*-dimethylformamide (50 ml) and pyridine (3.9 g, 50 mmol) were added trityl chloride (14.0 g, 50.4 mmol) and 4-(dimethylamino)pyridine (DMAP) (1.3 g, 10.5 mmol) at room temperature. The mixture was stirred at 70°C for 3 days, and then poured onto ice/water and extracted with ethyl acetate. The extract was washed with water, saturated copper (II) sulphate solution, water, and brine, dried with magnesium sulphate, and concentrated in vacuum. Compound **2j** was purified by flash chromatography over silica gel using cyclohexane/diethyl ether 9:1 as eluent with 50% yield (7.83 g).
(M^+, *Calcd* for $C_{22}H_{19}NO$: 313.1466 *Found* 313.1464), *m/e* 313 (M^+), 243, 236, 183, 165, 105 (base-peak), 77. IR: (film) 3080, 3020, 2960-2860, 2250, 1490, 1470, 1450. ^{1}H-NMR (90 MHz) 1.45 (d, 3 H J=6.0), 4.20 (q, 1 H J=6.0), 7.20-7.60 (m, 15 H).

Preparation of (*R,S*)- 2-(*t*-butyl)dimethylsilyloxy-decane-nitrile[24] 2o.

Obtained following the procedure described for compound **2p** (see below) starting from nonanal (2.6 ml, 15 mmol)). The intermediate **(*R,S*)- 2-trimethylsilyloxy-decan-nitrile 2t** is obtained by distillation of the crude reaction mixture (139°C 18 mm Hg) (1.93 g, 53 % yield).
(M^+, *Calcd* for $C_{13}H_{27}NOSi$: 241.1862 *Found* 241.1865), *m/e* 241 (M^+), 226, 199 (base-peak), 171, 143, 129, 101, 84, 75, 73, 55, 41. IR (film): 2980-2860, 2250, 1460, 1260. ^{1}H-NMR (90 MHz) 0.10 (s, 9 H), 0.60-0.80 (m, 3 H), 1.02-1.48 (m, 12 H), 1.50-1.77 (m, 2 H), 4.20 (t, 1 H J=6.0).
This compound was converted to the target **2o** following the procedure described for compound **2p** starting from (1.9 g, 8 mmol) of **2t**. Distillation in vacuo (145°C ,18 mm Hg) afforded **2o** (1.7 g, 76% yield).
(M^+, Calcd for $C_{16}H_{33}NOSi$: 283.2331 Found 283.2334), *m/e* 283 (M^+), 268, 226, 199 (base-peak), 115, 101, 75. IR (film): 2980-2860, 2250, 1460, 1260 .^{1}H-NMR (90 MHz) 0.28 (s, 3 H), 0.32 (s, 3 H), 1.00 (s, 9 H), 0.80-1.10 (m, 3 H), 1.20-1.60 (m, 12 H), 1.70-2.00 (m, 2 H), 4.47 (t, 1 H J=6.0)

Preparation of (*R,S*)- 2-(*t*-butyl)dimethylsilyloxy-(E)-3-pentene-nitrile[24] 2p

To 20 mmol of 2-butenale (1.4 g) contained in a dry two-necked reaction vessel fitted with a serum cap and a magnetic stirring bar, was added *via* a syringe 25 mmol of trimethylsilyl cyanide (3.3 ml) at 0°C

containing a catalytic amount of anhydrous zinc iodide with stirring. After 0.5 h the reaction was complete and the cyanohydrin was distilled directly from the reaction flask at 98°C (18 mm Hg) in 70 % yield (2.37 g). This compound was identified as **(*R,S*)- 2-trimethylsilyloxy-(E)-3-pentene-nitrile 2s.**
(M^+, *Calcd* for $C_8H_{15}NOSi$: 169.0923 *Found* 169.0926), *m/e* 169 (M^+), 154, 140, 127, 99, 84, 75, 73 (base-peak), 45. IR (film): 3040, 2960-2860, 2230, 1670, 1460. ^{1}H-NMR (90 MHz) 0.25 (s, 9 H), 1.76 (d, 3 H J=6.0), 4.90 (d, 1 H J=7.5), 5.50 (m, 1 H), 5.90 (m, 1 H).
The conversion of **2s** to the target was conducted as follow:

To a solution of compound **2s** (2.4 g, 14 mmol) in acetonitrile (40 ml) was added 2.5 ml of 40% HF aqueous solution at room temperature, and the mixture was stirred overnight. After quenching with saturated $NaHCO_3$ solution, extraction with CH_2Cl_2, drying over magnesium sulphate, concentration in vacuum, the crude containing 1-cyano-2-buten-1-ol was dissolved in *N,N*-dimethylformamide (15 ml) without further purification, and treated with TBDMSCl and imidazole to give compound **2p**, following the procedure previously described for compound **2a**. (*R,S*)-2-(*t*-butyl)dimethylsilyloxy-(E)-3-penten-nitrile **2p** was obtained after distillation in vacuo at 120 °C (18 mm Hg) in 69% yield (2.1 g).
(M^+, *Calcd* for $C_{11}H_{21}NOSi$: 211.1392 *Found* 211.1395), *m/e* 211 (M^+), 154, 127 (base-peak), 99, 75, 41. IR (film): 3040, 2960-2860, 2230, 1690, 1670, 1460. ^{1}H-NMR (90 MHz) 0.15 (s, 3 H), 0.18 (s, 3 H), 0.96 (s, 9 H), 1.78 (d, 3 H J=6.0), 4.90 (d, 1 H J=7.5), 5.55 (dd, 1 H), 5.90 (m, 1 H).

General procedure for the synthesis of 1,2-aminols protected as (*t*-butyl)dimethylsilylethers.

To a solution of cyanohydrin (2 mmol) in anhydrous *n*-pentane (10 ml) is added at -78°C under argon atmosphere diisobutylaluminium hydride (DIBAH, 2.2 mmol, 0.40 ml) dissolved in *n*-pentane (4 ml) and the mixture is stirred at the same temperature for 3-4 h. After disappearance of the starting material (t.l.c. monitoring), the organometallic reagent (4 mmol) is added and the reaction is allowed to reach room temperature while stirring was continued for 12-14 h. Quenching with a saturated potassium sodium tartrate solution and stirring until the two phases become clear (about 1 h), extraction with ethyl acetate, drying over magnesium sulfate, and concentration in vacuo gave the crude products. Subsequent flash chromatography on silica gel column eluting with $CHCl_3$:CH_3OH:NH_4OH (30% aqueous solution) 250:10:1 affords aminols.

1,2-*syn*- and 1,2-*anti*-2-amino-1-(*t*-butyl)dimethylsilyloxy-1-phenyl-4-pentene 4a and 5a
Obtained by the general procedure starting from **2a**, DIBAH and allyl lithium[29] 0.5 M in diethyl ether, in 43% yield (*Syn/anti* 91:9)
(M^+-15, *Calcd* for $C_{16}H_{26}NOSi$: 276.1784, *Found* 276.1788), *m/z* 276 (M^+-15), 250, 234, 221, 192, 163, 149, 118, 91, 73, 70 (base-peak). IR (film): 3380, 3080, 3020, 2980-2860, 1635, 1600, 1250.
***Syn* isomer 4a**: ^{1}H-NMR -0.23 (s, 3 H), 0.04 (s, 3 H), 0.90 (s, 9 H), 1.62 (bs, 2 H), 1.92 (m, 1 H), 2.12 (m, 1 H), 2.85 (m, 1 H), 4.45 (d, 1 H J=5.8), 5.00-5.15 (m, 2 H), 5.70-5.88 (m, 1 H), 7.20-7.37 (m, 5 H). ^{13}C-NMR 142.7, 135.8, 128.1, 127.5, 127.0, 117.1, 78.8, 57.7, 37.9, 25.7, 18.0, -4.7, -5.2.
***Anti* isomer 5a**: ^{1}H-NMR -0.21 (s, 3 H), 0.04 (s, 3 H), 0.89 (s, 9 H), 1.64 (bs, 2 H), 1.92 (m, 1 H), 2.47 (m, 1 H), 2.93 (m, 1 H), 4.48 (d, 1 H J=5.8), 5.00-5.15 (m, 2 H), 5.70-5.88 (m, 1 H), 7.20-7.37 (m, 5 H). ^{13}C-NMR 142.0, 136.0, 127.9, 127.3, 127.0, 117.3, 78.7, 57.1, 37.3, 25.7, 18.0, -4.6, -5.1.

1,2-*syn*- and 1,2-*anti*- 2-amino-1-(*t*-butyl)dimethylsilyloxy-1-phenyl-4-pentene 4a and 5a.
Obtained by the general procedure starting from **2a**, DIBAH and allyl magnesium chloride 2.0 M in THF, in 26% yield (*Syn/anti* 86:14)

1,2-*syn*- and 1,2-*anti*-2-amino-1-methoxy-1-phenyl-4-pentene 4b and 5b
Obtained by the general procedure starting from **2b** dissolved in THF, DIBAH and allyl magnesium chloride 2.0 M in THF, in 30% yield (*Syn/anti* 71:29)
(M^+-31, *Calcd* for $C_{11}H_{14}NO$: 160.1126, *Found* 160.1129), *m/z* 160 (M^+-31), 150, 128, 121, 118, 91, 77, 70 (base-peak). IR (film): 3380, 3080, 3020, 2980-2860, 1635, 1600, 1250

***Syn* isomer 4b**: ^{1}H-NMR 1.75 (bs, 2 H), 1.88 (m, 1 H), 2.04 (m, 1 H), 2.95 (m, 1 H), 3.20 (s 3 H), 3.89 (d 1 H J=6.9), 4.98-5.10 (m 2 H), 5.65-5.80 (m 1 H), 7.20-7.37 (m 5 H). ^{13}C-NMR 139.4, 135.3, 128.3, 127.8, 127.4, 117.5, 87.8 , 56.8, 56.0, 37.7.
***Anti* isomer 5b**: ^{1}H-NMR 1.75 (bs, 2 H), 1.88 (m, 1 H), 2.45 (m, 1 H), 3.00 (m, 1 H), 3.20 (s 3 H), 3.99 (d 1 H J=6.0), 5.04-5.12 (m, 2 H), 5.68-5.89 (m, 1 H), 7.20-7.37 (m, 5 H). ^{13}C-NMR 138.9, 135.7, 128.4, 127.9, 127.6, 117.6, 87.3, 56.9, 55.3, 37.6.

1,2-*syn*- and 1,2-*anti*-2-amino-1-(*t*-butyl)dimethylsilyloxy-1-phenyl-4-pentene 4a and 5a
Obtained by the general procedure starting from **2a** dissolved in *tert*-butyl methyl ether, DIBAH and allyl magnesium chloride 2.0 M in THF in 48% yield (Syn/anti 70:30)

1,2-*syn*- and 1,2-*anti*-2-amino-1-methoxy-1-phenyl-4-pentene 4b and 5b
Obtained by the general procedure starting from **2b** dissolved in *tert*-butyl methyl ether, DIBAH and allyl magnesium chloride 2.0 M in THF, in 56% yield (Syn/anti 67:33)

1,2-*syn*- and 1,2-*anti*-2-amino-1-(*t*-butyl)dimethylsilyloxy-1-phenyl-propane 4c and 5c
Obtained by the general procedure starting from **2a**, DIBAH and methyllithium 1.6 M in ether, in 29% yield (*Syn/anti* 75:25)
(M^+-15, *Calcd* for $C_{14}H_{24}NOSi$: 250.1627, *Found* 250.1620), *m/z* 250 (M^+-15), 221, 191, 149, 73, 44 (base-peak). IR (film): 3380, 3060, 2980-2860, 1600, 1460, 1450, 1250, 1160.
***Syn* isomer 4c**: ^{1}H-NMR -0.26 (s, 3 H), 0.00 (s, 3 H), 0.86 (s, 9 H), 0.93 (d, 3 H J=6.4), 1.45 (bs, 2 H), 2.92 (quintet, 1 H J=6.4), 4.29 (d, 1 H J= 6.4), 7.15-7.42 (m 5 H). ^{13}C-NMR 143.1, 128.0, 127.4, 126.9, 80.8, 53.8, 25.6, 19.2, 17.9, -4.9, -5.4.
***Anti* isomer 5c**: ^{1}H-NMR -0.21 (s, 3 H), 0.02 (s, 3 H), 0.86 (s, 9 H), 0.99 (d, 3 H J=6.5), 1.45 (bs, 2 H), 3.00 (quintet, 1 H J=6.5), 4.41 (d, 1 H J=6.5), 7.15-7.42 (m, 5 H). ^{13}C-NMR 142.1, 128.2, 128.0, 127.2, 80.1, 53.3, 25.6, 18.5, 17.9, -5.0, -5.2.

1,2-*syn*- and 1,2-*anti*- 2-amino-1-(*t*-butyl)dimethylsilyloxy-1-phenyl-hexane 4d and 5d
Obtained by the general procedure starting from **2a**, DIBAH and *n*-butyllithium 2.5 M in *n*-hexane, in 48% yield (*Syn/anti* 91:9)
(M^+-15, *Calcd* for $C_{17}H_{30}NOSi$: 292.2097, *Found* 292.2094), *m/z* 292 (M^+-15), 250, 233, 221, 176, 163, 149, 118, 86 (base-peak). IR (film): 3380, 3060, 3020, 2980-2860, 1600, 1470, 1460, 1450, 1250.
***Syn* isomer 4d**: ^{1}H-NMR -0.24 (s, 3 H), 0.02 (s, 3 H), 0.85 (s, 3 H), 0.88 (m, 9 H), 1.12-1.45 (m, 6 H), 1.40 (bs, 2 H), 2.70 (m, 1 H), 4.39 (d, 1 H J=5.3), 7.19-7.38 (m, 5 H). ^{13}C-NMR 144.4, 128.1, 127.4, 127.1, 79.7, 58.4, 33.3, 28.6, 25.8, 22.6, 18.1, 13.7, -4.6, -5.1 (Si-CH_3).
***Anti* isomer 5d**: ^{1}H-NMR -0.21 (s, 3 H), 0.02 (s, 3 H), 0.85 (s, 3 H), 0.87 (m, 9 H), 1.12-1.45 (m, 6 H), 1.40 (bs, 2 H), 2.84 (m, 1 H), 4.44 (d, 1 H J=5.1), 7.19-7.38 (m, 5 H). ^{13}C-NMR 143.4, 128.0, 127.4, 127.1, 79.6, 58.0, 32.6, 28.5, 25.8, 22.7, 18.1, 13.7, -4.8, -5.1.

1,2-*syn*- and 1,2-*anti*-2-amino-1-(*t*-butyl)dimethylsilyloxy-1-phenyl-3-methyl-pentane 4e and 5e
Obtained by the general procedure starting from **2a**, DIBAH and *s*-butyllithium 1.4 M in *n*-hexane in 45% yield (*Syn/anti* 67:33). The relative configuration of the C-3 carbon stereocentre has not been determined. (*1° Syn* isomer:*2° Syn* isomer 50:50) (*1° Anti* isomer:*2° Anti* isomer 50:50)
(M^+-15, *Calcd* for $C_{17}H_{30}NOSi$: 292.2097, *Found* 292.2099), *m/z* 292 (M^+-15), 250, 233, 221, 192, 163, 149, 118, 86 (base-peak), 73. IR (film): 3380, 3060, 3020, 2980-2860, 1600, 1470, 1460, 1450, 1250.
***1° Syn* isomer 4e**: ^{1}H-NMR -0.26, (s, 3 H), 0.05, (s, 3 H), 0.88, (s , 9 H), 0.80-0.99 (m, 5 H), 1.10-1.45 (m, 5 H), 1.62 (m, 1 H), 2.58 (t, J=5.2), 4.64 (d, J=5.2), 7.22-7.38 (m, 5 H). ^{13}C-NMR 143.5, 128.2, 127.6, 127.1, 77.6, 61.0, 35.7, 27.5; 25.7, 23.7, 17.0, 11.4, -4.7, -5.3.

2° *Syn* isomer 4e: ^{1}H-NMR -0.24 (s, 3 H), 0.05, (s, 3 H), 0.89 (s , 9 H), 0.80-0.99 (m, 5 H), 1.10-1.45 (m, 5 H), 1.62 (m, 1 H), 2.79 (dd, J=7.1, 3.4), 4.49 (d, J=7.1), 7.22-7.38 (m, 5 H). ^{13}C-NMR 143.9, 128.2, 127.6, 127.1, 78.4, 63.4, 34.8, 27.5; 25.7, 23.7, 17.9, 13.1, -4.6, -5.3.
1° *Anti* isomer 5e: ^{1}H-NMR -0.27, (s, 3 H), 0.03, (s, 3 H), 0.90, (s, 9 H), 0.80-0.99 (m, 5 H), 1.10-1.45 (m, 5 H), 1.85 (m, 1 H), 2.79 (dd, J=7.1, 3.4), 4.56 (d, J=7.1), 7.22-7.38 (m, 5 H). ^{13}C-NMR 143.0, 127.6, 127.3, 126.5, 77.6, 62.8, 34.6, 25.6, 27.6, 22.5, 17.9, 12.5, -4.9, -5.5.
2° *Anti* isomer 5e: ^{1}H-NMR -0.25 (s, 3 H), 0.03, (s, 3 H),0.91 (s, 9 H), 0.80-0.99 (m, 5 H), 1.10-1.45 (m, 5 H), 1.85 (m, 1 H), 2.86 (dd, J=7.6, 3.2), 4.45 (d, J=7.6), 7.22-7.38 (m, 5 H). ^{13}C-NMR 143.2, 127.6, 127.3, 126.5, 78.4, 60.3,34.2, 25.6, 27.6, 22.5, 17.0, 11.8, -4.8, -5.5.

1,2-*syn*- and 1,2-*anti*-2-amino-1-(*t*-butyl)dimethylsilyloxy-1-phenyl-3,3-dimethyl-butane 4f and 5f
Obtained by the general procedure starting from **2a**, DIBAH and *t*-butyllithium 1.5 M in *n*-hexane, in 27% yield (*Syn/anti* 12:88)
(M^+-15, *Calcd* for $C_{17}H_{30}NOSi$: 292.2097, *Found* 292.2097), *m/z* 292 (M^+-15), 250, 221, 177, 163, 149, 119, 118, 86 (base-peak), 73. IR (film): 3380, 3060, 2980-2860, 1600, 1460, 1450, 1250
***Syn* isomer 4f:** ^{1}H-NMR -0.28 (s, 3 H), 0.05 (s, 3 H), 0.87 (s, 9 H), 0.92 (s, 9 H), 1.35 (bs, 2 H), 2.83 (d, 1 H J=5.1), 4.76 (d, 1 H J=5.1), 7.20-7.45 (m, 5 H). ^{13}C-NMR 143.0, 128.4, 128.0, 127.6, 76.6; 66.2; 33.5, 27.2, 25.7, 17.8, -4.8, -5.2.
***Anti* isomer 5f:** ^{1}H-NMR -0.35 (s, 3 H), 0.12 (s, 3 H), 0.96 (s, 9 H), 1.03 (s, 9 H), 1.89 (bs, 2 H), 2.31 (d, 1 H J=1.7), 4.99 (d, 1H J=1.7), 7.20-7.45 (m, 5 H). ^{13}C-NMR 145.5, 128.1, 127.2, 126.5, 73.7, 66.5, 34.4, 27.3, 25.8, 17.8, -4.2, -4.9.

1,2-*syn*- and 1,2-*anti*- 2-amino-1-(*t*-butyl)dimethylsilyloxy-1-phenyl-heptane 4g and 5g
Obtained by the general procedure starting from **2a**, DIBAH and pentyllithium[30] 1.0 M in ether, in 40% yield (*Syn/anti* 87:13)
(M^+-15, *Calcd* for $C_{18}H_{32}NOSi$: 306.2253, *Found* 306.2252), *m/z* 306 (M^+-15), 264, 247, 221, 163, 149, 100 (base-peak), 73. IR (film): 3380, 3060, 2980-2860, 1600, 1460, 1450, 1250, 1160.
***Syn* isomer 4g:** ^{1}H-NMR -0.23 (s, 3 H), 0.03 (s, 3 H), 0.78-0.92 (m, 5 H), 0.89 (s, 9 H) 1.15-1.33 (m, 6 H), 1.51 (bs, 2 H), 2.71 (m, 1 H), 4.40 (d, 1 H J=5.4,) 7.22-7.36 (m, 5 H). ^{13}C-NMR 143.3, 128.1, 127.4, 127.0, 79.2, 58.3, 33.4, 31.7, 26.0, 25.7, 22.4, 17.9, 13.8, -4.3, -4.7.
***Anti* isomer 5g:** ^{1}H-NMR -0.19 (s, 3 H), 0.03 (s, 3 H), 0.78-0.92 (m, 5 H), 0.88 (s, 9 H), 1.15-1.33 (m, 6 H), 1.51 (bs, 2 H), 2.82 (m, 1 H), 4.45 (d, 1 H J=5.4), 7.19-7.38 (m, 5 H). ^{13}C-NMR 142.3, 128.0, 127.4, 127.0, 79.1, 57.9, 32.6, 31.9, 26.0, 25.7, 22.4, 17.9, 13.8, -4.3, -4.7.

1,2-*syn*- and 1,2-*anti*- 2-amino-1-(*t*-butyl)dimethylsilyoxy-1-phenyl-octane 4h and 5h
Obtained by the general procedure starting from **2a**, DIBAH and hexyllithium[25] 1.5 M in ether, in 35% yield (*Syn/anti* 81:19)
(M^+-15, Calcd for $C_{19}H_{34}NOSi$: 320.2410, Found 320.2398), *m/z* 320 (M^+-15), 278, 261, 250, 233, 221, 163, 149, 114 (base-peak), 86, 73. IR (film): 3380, 3060, 2980-2860, 1600, 1460, 1450, 1250, 1160.
***Syn* isomer 4h:** ^{1}H-NMR -0.24 (s, 3 H), 0.02 (s, 3 H), 0.75-0.96 (m, 5 H), 0.89 (s, 9 H), 1.12-1.33 (m, 8 H), 1.45 (bs, 2 H), 2.71 (m, 1 H), 4.40 (d, 1 H J=5.4), 7.20-7.45 (m, 5 H). ^{13}C-NMR 143.4, 128.1, 127.4, 127.0, 79.3, 58.3, 33.4, 31.6, 29.1, 26.3, 25.7, 22.4, 18.0, 13.8, -4.8, -5.3.
***Anti* isomer 5h:** ^{1}H-NMR -0.19 (s, 3 H), 0.02 (s, 3 H), 0.75-0.96 (m, 5 H), 0.89 (s, 9 H), 1.12-1.33 (m, 8 H), 1.45 (bs, 2 H), 2.82 (m, 1 H), 4.49 (d, 1 H J=5.1) 7.20-7.45 (m, 5 H. ^{13}C-NMR 143.2, 128.0, 127.4, 127.0, 79.3, 57.9, 32.6, 31.5, 29.1, 26.3, 25.7, 22.4, 18.0, 13.8, -4.8, -5.3.

2,3-*syn*- and 2,3-*anti*-3-amino-2-(*t*-butyl)dimethylsilyloxy-heptane 4i and 5i

Obtained by the general procedure starting from **2i**, DIBAH and *n*-butyllithium 1.6 M in *n*- hexane, in 57% yield (*Syn/anti* 76:24)
(M^+-15, *Calcd* for $C_{12}H_{28}NOSi$: 230.1940, *Found* 230.1942), *m/z* 230 (M^+-15), 188, 171, 159, 115, 86 (base-peak), 73. IR (film): 3380, 3300, 2980-2860, 1580, 1250, 1070.
Syn **isomer 4l**: ^{1}H-NMR 0.05 (bs, 6 H), 0.82-0.94 (m, 12 H), 1.12 (d, 3 H J=6.2) 1.17-1.50 (m, 8 H), 2.46 (m, 1 H), 3.59 (m, 1 H). ^{13}C-NMR 71.7, 57.3, 33.7, 28.6, 25.8, 22.8, 20.5, 18.0, 14.0, -4.2, -4.8.
Anti **isomer 5i**: ^{1}H-NMR 0.04 (s, 6 H), 0.82-0.94 (m, 12 H), 1.03 (d, 3 H J=6.2), 1.17-1.50 (m, 8 H), 2.66 (m, 1 H), 3.69 (m, 1 H). ^{13}C-NMR 71.3, 56.8, 32.6, 28.7, 25.7, 22.8, 18.0, 16.8, 14.0, -4.5, -4.9.

2,3-*syn*- and 2,3-*anti*-3-amino-2-(t-butyl)dimethylsilyloxy-4,4-dimethylpentane 4k and 5k
Obtained by the general procedure starting from **2i**, DIBAH and *t*-butyllithium 1.6 M in *n*-hexane, in 60% yield (*Syn/anti* 45:55)
(M^+-15, *Calcd* for $C_{12}H_{28}NOSi$: 230.1940, *Found* 230.1942), *m/z* 230 (M^+-15), 188, 172, 159, 118, 86 (base-peak), 73. IR (film): 3380, 2980-2860, 1580, 1460, 1250, 1070.
Syn **isomer 4k**: ^{1}H-NMR 0.07 (s, 3 H), 0.08 (s, 3 H), 0.88 (s, 9 H), 0.92 (s, 9 H), 1.20 (d, 3 H J=6.3 Hz), 1.33 (bs, 2 H), 2.07 (d, 1 H J=1.2), 4.17 (dq, 1 H J=6.3, 1.2). ^{13}C-NMR 67.3, 65.3, 34.4, 27.1, 25.8, 23.5, 17.8, -3.5, -4.6.
Anti **isomer 5k**: ^{1}H-NMR 0.03 (s, 3 H), 0.04 (s, 3 H), 0.87 (s, 9 H), 0.93 (s, 9 H), 1.06 (d, 3 H J=6.3), 1.40 (bs, 2 H), 2.56 (d, 1 H J=2.7), 4.00 (dq, 1 H J=6.3, 2.7). ^{13}C-NMR 68.9, 65.6, 32.9, 27.3, 25.6, 17.7, 17.5, -4.9, -5.1.

1,2-*syn*- and 1,2-*anti*-1-amino-1-cyclopropyl-2-(*t*-butyl)dimethylsilyloxy-propane 4l and 5l.
Obtained by the general procedure starting from **2i**, DIBAH and cyclopropyllithium[25] 0.7 M in ether, in 40% yield (*Syn/anti* 86:14)
(M^+-15, *Calcd* for $C_{11}H_{24}NOSi$: 214.1627 *Found* 214.1630), *m/z* 214 (M^+-15), 172, 155, 116, 115, 75, 74, 73, 70 (base-peak), 43. IR (film): 3380, 2980-2860, 1580, 1460, 1250, 1070.
Syn **isomer 4l**: ^{1}H-NMR 0.00 (s, 3 H), 0.08 (s 3 H), 0.20 (m, 2 H), 0.50 (m, 2 H), 0.75 (m, 1 H), 0.90 (s, 9 H), 1.20 (d, 3 H J=6.3), 1.62 (bs, 2 H), 1.75 (dd, 1 H J=9.1, 5.2), 3.78 (dq, 1 H J=6.3, 5.2). ^{13}C-NMR 72.6, 62.9, 25.6, 20.8, 17.7, 15.6, 3.5, 2.4, -4.5, -5.1.
Anti **isomer 5l**: ^{1}H-NMR -0.01 (s, 3 H), 0.07 (s, 3 H), 0.20 (m, 2 H), 0.50 (m, 2 H), 0.75 (m, 1 H), 0.89 (s, 9 H), 1.17 (d, 3 H J=6.3), 1.62 (bs, 2 H), 1.95 (dd, 1 H J=9.3, 3.0), 3.89 (m, 1 H). ^{13}C-NMR 72.1, 62.1, 25.6, 17.8, 17.7, 13.6, 3.1, 2.0, -4.8, -5.2.

2,3-*syn*- and 2,3-*anti*-3-amino-2-(*t*-butyl)dimethylsilyloxy-5-hexene 4m and 5m
Obtained by the general procedure starting from **2i**, DIBAH and allyllithium 0.33 M in ether, in 47% yield (*Syn/anti* 71:29)
(M^+-15, *Calcd* for $C_{11}H_{24}NOSi$: 214.1627 *Found* 214.1622), *m/z* 214 (M^+-15), 188, 172, 130, 115, 73, 70 (base-peak), 43. IR (film): 3380, 3280, 3080, 2990-2850, 1640, 1570, 1250, 1100.
Syn **isomer 4m**: ^{1}H-NMR 0.06 (s, 6 H), 0.89 (s, 9 H), 1.15 (d, 3 H J=6.2), 1.49 (bs, 2 H), 1.99 (m, 1 H), 2.28 (m, 1 H), 2.59 (m, 1 H), 3.67 (quintet, 1H J=6.2), 5.07-5.18 (m, 2 H), 5.75-5.90 (m, 1 H). ^{13}C-NMR 136.4, 117.0, 71.5, 56.8, 38.7, 25.6, 20.2, 17.8, -4.4, -5.1.
Anti **isomer 5m**: ^{1}H-NMR 0.05 (s, 6 H), 0.88 (s, 9 H), 1.09 (d, 3 H J=6.2), 1.49 (bs, 2 H), 1.99 (m, 1 H), 2.28 (m, 1 H), 2.74 (m, 1 H), 3.73 (m, 1 H), 5.07-5.18 (m, 2 H), 5.75-5.90 (m, 1 H). ^{13}C-NMR 136.1, 116.8, 71.5, 56.3, 37.6, 25.7, 17.9, 17.9, -4.5, -5.1.

2,3-*syn*- and 2,3-*anti*-3-amino-2-(*t*-butyl)dimethylsilyloxy-5-hexene 4m and 5m
Obtained by the general procedure starting from **2i**, DIBAH and allylmagnesium chloride 2.0 M in THF, in 44% yield (*Syn/anti* 65:35)

4,5-*syn*- and 4,5-*anti*-4-amino-5-(*t*-butyl)dimethylsilyloxy-1-tridecene 4o and 5o
Obtained by the general procedure starting from **2o**, DIBAH and allylmagnesium chloride 2.0 M in THF, in 50% yield (*Syn/anti* 51:49)
(M^+-15, *Calcd* for $C_{18}H_{38}NOSi$: 312.2722, *Found* 312.2728), *m/z* 312 (M^+-15), 286, 270, 257, 228, 196, 130, 115, 75, 74, 73, 70 (base-peak). IR (film): 3380, 3280, 3080, 2990-2850, 1640, 1570, 1250, 1100.
***Syn* isomer 4o**: ^{1}H-NMR 0.06 (s, 6 H), 0.90 (s, 9 H), 0.82-0.96 (m, 3 H), 1.15-1.60 (m, 16 H), 1.98 (m, 1 H), 2.22 (m 1 H), 2.71 (m 1 H), 3.53 (m 1 H), 5.05-5.15 (m, 2 H), 5.72-5.90 (m, 1 H). ^{13}C-NMR 136.7, 117.0, 75.3, 53.6, 39.0, 33.4, 31.7, 29.7, 29.4, 29.1, 25.7, 25.1, 22.4, 17.9, 13.8, -4.4, -4.7.
***Anti* isomer 5o**: ^{1}H-NMR 0.06 (s, 6 H), 0.90 (s, 9 H), 0.82-0.96 (m, 3 H), 1.15-1.60 (m, 16 H), 1.98 (m, 1 H), 2.22 (m, 1 H), 2.82 (m, 1 H), 3.58 (m, 1 H), 5.05-5.15 (m, 2 H), 5.72-5.90 (m, 1 H). ^{13}C-NMR 136.5, 117.1, 75.6, 54.7, 37.4, 31.7, 31.2, 29.6, 29.4, 29.1, 25.7, 25.3, 22.4, 17.9, 13.8, -4.6, -4.8.

4,5-*syn*- and 4,5-*anti*-5-amino-4-(*t*-butyl)dimethylsilyloxy-2-nonene 4p and 5p
Obtained by the general procedure starting from **2p**, DIBAH and *n*-butyllithium 2.5 M in *n*-hexane, in 30% yield (*Syn/anti* 90:10)
(M^+-15, *Calcd* for $C_{14}H_{30}NOSi$: 256.2096, *Found* 256.2092), *m/z* 256 (M^+-15), 214, 197, 172, 143, 129, 113, 86 (base-peak), 73. IR (film): 3380, 3280, 3080, 2990-2850, 1640, 1570, 1250, 1100.
***Syn* isomer 4p**: ^{1}H-NMR 0.00 (s, 3 H), 0.04 (s, 3 H), 0.87 (s, 3 H), 0.89 (m, 9 H), 1.10-1.55 (m, 8 H), 1.70 (dd, 3 H J=6.3, 1.2), 2.53 (ddd, 1 H J=8.6, 5.2, 3.7), 3.81 (dd, 1 H J=6.9, 5.2), 5.40 (m, 1 H), 5.58 (m, 1 H). ^{13}C-NMR 132.6, 127.4, 77.8, 56.4, 33.1, 28.5, 25.7, 22.6, 17.9, 17.5, 13.8, -4.2, -5.1,
***Anti* isomer 5p**: ^{1}H-NMR 0.01 (s, 3 H), 0.03 (s, 3 H), 0.87 (m, 3 H), 0.91 (s, 9 H), 1.10-1.55 (m, 8 H), 1.67 (dd, 3 H J=6.3, 1.2), 2.67 (m, 1 H), 3.90 (dd, 1 H J=6.3, 4.2), 5.40 (m, 1), 5.58 (m 1 H). ^{13}C-NMR 132.7, 127.9, 77.2, 56.5, 32.6, 28.5, 25.5, 22.7, 17.9, 17.6, 13.8, -3.8, -4.5.

4,5-*syn*- and 4,5-*anti*-5-amino-4-(*t*-butyl)dimethylsilyloxy-7-methyl-2-octene 4q and 5q.
Obtained by the general procedure starting from **2p**, DIBAH and *i*-butyllithium[25] 1.0 M in ether, in 36% yield (*Syn/anti* 88:12)
(M^+-15, *Calcd* for $C_{14}H_{30}NOSi$: 256.2096, *Found* 256.2094), *m/z* 256 (M^+-15), 214, 197, 185, 155, 140, 129, 113, 86 (base-peak), 75, 74, 73. IR (film): 3380, 3280, 3080, 2990-2850, 1640, 1570, 1250, 1100.
***Syn* isomer 4q**: ^{1}H-NMR 0.00 (s, 3 H), 0.04 (s, 3 H), 0.89 (s, 9 H), 0.89 (d, 3 H J=6.6), 0.90 (m, 1 H), 0.91 (d, 3 H J=6.6), 1.05-1.27 (m, 2 H), 1.47 (bs, 2 H), 1.70 (dd, 3 H J=6.1, 1.2), 2.63 (ddd, 1 H J=9.4, 5.1, 4.3 Hz), 3.78 (dd, 1 H J=6.8, 5.1), 5.40 (m, 1 H), 5.59 (m, 1 H). ^{13}C-NMR 132.5, 127.4, 78.0, 54.0, 42.6, 25.6, 24.4, 23.5, 21.4, 17.9, 17.4, -4.3, -5.2.
***Anti* isomer 5q**: ^{1}H-NMR 0.02 (s, 3 H), 0.03 (s, 3 H), 0.89 (d, 3 H J=6.6), 0.90 (m, 1 H), 0.91 (s, 9 H), 0.91 (d, 3 H J=6.6), 1.16 (m, 2 H), 1.47 (bs, 2 H), 1.67 (dd, 3 H J=6.1, 1.2), 2.76 (m, 1 H), 3.88 (dd, 1 H J=6.8, 4.5), 5.40 (m, 1 H), 5.59 (m, 1 H). ^{13}C-NMR 132.6, 127.8, 77.3, 54.2, 42.2, 25.5, 24.4, 23.4, 21.3, 17.9, 17.5, -4.6, -5.3.

4,5-*syn*- 4,5-*anti*-5-amino-4-(*t*-butyl)dimethylsilyloxy-2,7-octadiene 4r and 5r.
Obtained by the general procedure starting from **2p**, DIBAH and allylmagnesium chloride 2.0 M in THF, in 30% yield (*Syn/anti* 77:23)
(M^+-15, *Calcd* for $C_{13}H_{26}NOSi$: 240.1783, *Found* 240.1788), *m/z* 240 (M^+-15), 198, 185, 129, 114, 73 (base-peak), 70
***Syn* isomer 4r**: ^{1}H-NMR 0.00 (s, 6 H), 0.90 (s, 9 H), 1.53 (bs, 2 H), 1.70 (dd, 3 H J=6.3, 1.2), 1.85-2.10 (m, 2 H), 2.66 (ddd, 1 H J=9.1, 5.2, 4.1), 3.86 (dd, 1 H J=6.3, 5.2), 5.02-5.17 (m, 2 H), 5.41 (m, 1 H), 5.62 (m, 1 H), 5.70-5.90 (m, 1 H). ^{13}C-NMR 136.4, 132.3, 127.8, 117.1, 77.4, 56.0, 38.0, 25.7, 17.9, 17.4, -4.2, -5.1.
***Anti* isomer 5r**: ^{1}H-NMR 0.00 (s, 6 H), 0.89 (s, 9 H), 1.53 (bs, 2 H), 1.72 (dd, 3 H J=6.3, 1.2), 1.88 (m, 1 H), 2.30 (m, 1 H), 2.74 (m, 1 H), 3.91 (dd, 1 H J=6.3, 4.5), 5.02-5.17 (m, 2 H), 5.43 (m, 1 H), 5.62 (m,

1 H), 5.70-5.90 (m, 1 H). ^{13}C-NMR 136.4, 131.0, 128.2, 117.2, 77.2, 55.7, 37.4, 25.6, 17.9, 17.5, -4.4, -5.2.

Synthesis of 1,2-aminols protected as tritylethers

To a solution of cyanohydrin (1.5 mmol) in toluene (5 ml), is added DIBAH (0.30 ml, 1.65 mmol) dissolved in anhydrous *n*-pentane (4 ml) at -78°C under argon atmosphere, and the mixture is stirred for 1 h, following the reaction by t.l.c., IR or GC. After disappearance of the starting material, the organometallic reagent (4 mmol) is added and the reaction is allowed to reach room temperature while stirring is continued for 12-14 h. Quenching with a saturated potassium sodium tartrate solution and stirring until the two phases become clear (about 1 h), extraction with ethyl acetate, drying over magnesium sulfate, and concentration in vacuo gave the crude products. Subsequent flash chromatography on silica gel column eluting with $CHCl_3$:CH_3OH:30% NH_4OH aqueous solution 250:10:1 affords aminols.

2,3-*syn*- and 2,3-*anti*-3-amino-2-triphenylmethoxy-heptane 4j and 5j

Obtained by the general procedure starting from **2j**, DIBAH and *n*-butyllithium 2.5 M in *n*-hexane, in 70% yield (*Syn/anti* 85:15)

(*Found* H 8.43 C 83.5 N 3.79, $C_{26}H_{31}NO$ requires H 8.37 C 83.6 N 3.75), *m/z* 243 (CPh_3), 215, 189, 165, 139, 86 (base-peak). IR (film): 3380, 3080, 2980-2860, 1470, 1460, 1450.

***Syn* isomer 4j**: ^{1}H-NMR 0.85 (d, 3 H J=6.3), 0.70-0.90 (m, 3 H), 0.93-1.60 (m, 8 H), 2.28 (m, 1 H), 3.27 (dq, 1 H J=6.3, 4.4), 7.10-7.50 (m, 15 H). ^{13}C-NMR 145.5, 129.1, 127.7, 127.0, 73.5, 55.6, 32.0, 28.5, 22.5, 16.5, 13.8.

***Anti* isomer 5j**: ^{1}H-NMR 0.84 (d, 3 H J=6.2), 0.70-0.90 (m, 3 H), 0.93-1.70 (m, 8 H), 2.12 (m 1 H), 3.56 (m 1 H), 7.10-7.50 (m 15 H). ^{13}C-NMR 145.4, 129.1, 127.8, 127.1, 72.5, 54.3, 33.0, 28.4, 22.4, 13.8, 13.6.

2,3-*syn* and 2,3-*anti*-3-amino-2-triphenylmethoxy-5-hexene 4n and 5n.

Obtained by the general procedure starting from **2j**, DIBAH and allylmagnesium chloride 2.0 M in THF, in 56% yield (*Syn/anti* 65:35)

(*Found* H 7.70 C 83.92 N 3.87, $C_{25}H_{27}NO$ requires H 7.61 C 83.99 N 3.92), *m/z* 243 (CPh_3), 215, 165, 70 (base-peak). IR (film) 3380, 3080, 3020, 2980-2860, 1470, 1460, 1450, 1300.

***Syn* isomer 4n**: ^{1}H-NMR 0.92 (d, 3 H J=6.3), 1.70 (bs, 2 H), 1.87 (m, 2 H), 2.22 (m, 1 H), 3.57 (dq, 1 H J=6.3, 3.1), 4.90-5.01 (m, 2 H), 5.41-5.54 (m, 1 H), 7.20-7.60 (m, 15 H). ^{13}C-NMR 145.4, 135.9, 129.1, 127.8, 127.1, 116.7, 72.4, 54.0, 37.8, 14.2.

***Anti* isomer 5n**: ^{1}H-NMR 0.91 (d, 3 H J=6.3), 1.70 (bs, 2 H), 1.87 (m, 2 H), 2.40 (m, 1 H), 3.40 (m, 1 H), 4.99-5.08 (m, 2 H), 5.57-5.70 (m, 1 H), 7.20-7.60 (m, 15 H). ^{13}C-NMR 145.5, 136.6, 129.1, 128.0, 127.1, 116.9, 73.1, 54.8, 37.0, 16.3.

Synthesis of 1,2-aminols in the presence of Lewis acids.

To a solution of cyanohydrin (2 mmol,) in anhydrous *n*-pentane (10 ml), was added DIBAH (2.2 mmol, 0.40 ml) dissolved in *n*-pentane (4 ml) at -78°C under argon atmosphere, and the mixture was stirred for 3-4 h. After disappearance of the starting material and elimination of the solvent in vacuo, THF (15 ml) was added to dissolve the aluminium-imine and the temperature lowered to -78°C. To this solution Lewis acid (4 mmol) in THF (5 ml) was added dropwise and after 30 minutes the organometallic reagent in THF (4 mmol). The reaction was allowed to reach room temperature while stirring continued for 12-14 h. Quenching with a saturated sodium bicarbonate solution, extraction with ethyl acetate, drying over magnesium sulfate, and concentration in vacuo gave the crude products. Aminols were successively purified by flash chromatography on silica gel eluting $CHCl_3$:CH_3OH: 30% NH_4OH aqueous solution 250:10:1.

1,2-*syn*- 1,2-*anti*-2-amino-1-(*t*-butyl)dimethylsilyloxy-1-phenyl-4-pentene 4a and 5a

Obtained by the previously described procedure starting from **2a**, DIBAH and allyl magnesium chloride 2.0 M in THF in presence of $CeCl_3$, in 36% yield (*Syn/anti* 83:17),
Obtained by the previously described procedure starting from **2a**, DIBAH and allyl magnesium chloride 2.0 M in THF in presence of MgI_2, in 30% yield (*Syn/anti* 75:25)
Obtained by the previously described procedure starting from **2a**, DIBAH and allyl magnesium chloride 2.0 M in THF in presence of $ZnBr_2$, in 40% yield (*Syn/anti* 60:40)
Obtained by the previously described procedure starting from **2a**, DIBAH and allyl magnesium chloride 2.0 M in THF in presence of $BF_3{\cdot}Et_2O$, in 51% yield (*Syn/anti* 50:50)
Obtained by the previously described procedure starting from **2a**, DIBAH and allyl magnesium chloride 2.0 M in THF/CuI (1:1) in presence of $BF_3{\cdot}Et_2O$, in 41% yield (Syn/anti 66:34)

2,3-*syn*- and 2,3-*anti*-3-amino-2-(*t*-butyl)dimethylsilyloxy-5-hexene 4m and 5m
Obtained by the previously described procedure starting from **2i**, DIBAH and allyl magnesium chloride 2.0 M in THF in presence of $ZnBr_2$ in 43% yield (*Syn/anti* 60:40)
Obtained by the previously described procedure starting from **2i**, DIBAH and allyl magnesium chloride 2.0 M in THF/CuI (1:1) in presence of $BF_3{\cdot}Et_2O$, in 30% yield (Syn/anti 66:34)
2,3-*syn*- and 2,3-*anti* -3-amino-2-triphenylmethoxy-5-hexene 4n and 5n
Obtained by the previously described procedure starting from **2j** dissolved in toluene, DIBAH and allyl magnesium chloride 2.0 M in THF in presence of $BF_3{\cdot}Et_2O$, in 60% yield (*Syn/anti* 50:50)
1,2-*syn*- and 1,2-*anti*-2-amino-1-methoxy-1-phenyl-4-pentene 4b and 5b
Obtained by the previously described procedure starting from **2b**, DIBAH and allyl magnesium chloride 2.0 M in THF in presence of $BF_3{\cdot}Et_2O$, in 10% yield (*Syn/anti* 50:50)
Obtained by the previously described procedure starting from **2b**, DIBAH and allyl magnesium chloride 2.0 M in THF in presence of Et_2AlCl, in 16% yield (*Syn/anti* 58:42)

General procedure for the synthesis of 1,3-oxazolidin-2-ones from *O*-(*t*-butyl)dimethylsilyl-aminols
To a solution of *O*-protected aminol (1 mmol) in dioxane (15 ml) is added 1 ml of 1 M NaOH aqueous solution and di-*t*-butylcarbonate [$(BOC)_2O$] (1.1 mmol) at 0°C, and the mixture is stirred for 3-4 h. Then the reaction is poured onto a saturated $NaHCO_3$ solution, extracted with ethyl acetate, dried over $MgSO_4$, and concentrated in vacuo. The crude so obtained containing the N-BOC-*O*-protected aminols, is used for the next step without further purification; it is dissolved in dry THF (15 ml) under argon atmosphere, and to this solution is added tetrabutylammonium fluoride (TBAF) 1.0 M in THF (1.5 ml) and the stirring is continued for 12 h. The reaction work-up is the same described previously. The crude products containing N-BOC-aminols are cyclized using the procedure described next. In a reaction flask NaH dispersion (60% in mineral oil) (1.1 mmol, 0.044 g) is placed and washed with olefine-free *n*-pentane (2 x 5 ml); then DMF (10 ml) is added and this suspension is treated with a solution of the N-BOC aminols in DMF. After few hours the reaction is quenched with a saturated ammonium chloride solution, the resulting mixture is extracted with ether, and the extracts are dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography on a silica gel column of the resultant oil eluting with $CHCl_3$:CH_3OH:NH_4OH 30% aqueous solution 250:10:1 gives the title compounds. Since the preparation of the oxazolidin-2-ones were performed only for diagnostic use, the yields were not optimized. Usually on the three steps procedure the yields of the target were on the 30-50% range.

4,5-*trans*- and 4,5-*cis*-4-allyl-5-phenyl-1,3-oxazolidin-2-one 10a and 11a
(M^+-41, *Calcd* for $C_9H_8NO_2$: 162.0555, *Found* 162.0553), *m/z* 161 (M^+-41), 118, 107,91, 79, 77. IR (nujol): 3300, 3080, 2980, 2940, 1740, 1640, 1390.
***Trans* isomer 10a**: ^{1}H-NMR 2.43 (m, 1 H), 2.50 (m, 1 H), 3.80 (q, 1 H J=6.0), 5.18 (d, 1 H J=6.0), 5.21-5.28 (m, 2 H), 5.70-5.86 (m, 1 H), 5.84 (bs, 1H), 7.30-7.46 (m, 5 H). ^{13}C-NMR 159.2, 138.5, 132.3, 129.2, 129.1, 126.0, 119.8, 82.7, 59.8 , 39.0

***Cis* isomer 11a**: ^{1}H-NMR 1.76 (m, 2 H), 4.07 (q, 1 H J=8.0), 4.99-5.13 (m, 2 H), 5.49-5.65 (m, 1 H), 5.67 (bs, 1 H), 5.77 (d, 1 H J=8.0), 7.30-7.46 (m, 5H). ^{13}C-NMR 159.4, 134.9, 133.1, 128.8, 128.7, 126.3, 119.2, 80.5, 56.0, 36.1.

4,5-*trans* and 4,5-*cis*-4-butyl-5-phenyl-1,3-oxazolidin-2-one 10b and 11b
(M^+, *Calcd* for $C_{13}H_{17}NO_2$: 219.1259, *Found* 219.1262), *m/e* 219 (M^+), 162, 118 (base-peak), 107, 91, 79, 77, 57. IR (nujol): 3220, 3140, 2980-2860, 1725, 1460, 1380, 1240
***Trans* isomer 10b**: ^{1}H-NMR 0.92 (t, 3 H J=6.9), 1.33-1.47 (m, 4 H), 1.70 (m, 2 H), 3.74 (q, 1 H J=6.4), 5.13 (d, 1 H J=6.4), 6.72 (bs, 1 H), 7.32-7.47 (m, 5 H). ^{13}C-NMR 159.7, 138.6, 129.0, 126.1, 83.7, 60.8, 34.5, 27.4, 22.2, 13.5.
***Cis* isomer 11b**: ^{1}H-NMR: 0.92 (t, 3 H J=6.9), 1.33-1.47 (m, 4 H), 1.80 (m, 2 H), 4.03 (m, 1 H), 5.71 (d, 1 H J=8.1), 6.65 (bs 1 H), 7.32-7.47 (m 5 H). ^{13}C-NMR 160.3, 135.2, 128.4 , 126.2, 81.0, 57.0, 31.4, 27.2, 22.1, 13.5

4,5-*trans*- and 4,5-*cis*- 4-*s*-butyl-5-phenyl-1,3-oxazolidin-2-one 10c and 11c
(M^+, *Calcd* for $C_{13}H_{17}NO_2$: 219.1259, *Found* 219.1257), *m/e* 219 (M^+), 162, 118 (base-peak), 107, 91, 79, 77, 57. IR (nujol): 3220, 3140, 2980-2860, 1725, 1460, 1380, 1240.
***1° Trans* isomer 10c**: ^{1}H-NMR 0.82-1.10 (m, 8 H), 1.63 (m, 1 H), 3.64 (dd, J=6.3, 4.8), 5.24 (d, J=4.8), 6.37 (bs, 1 H), 7.25-7.45 (m, 5 H). ^{13}C-NMR 159.7, 139.5, 128.9, 128.8, 125.9, 125.8, 81.5, 64.8, 39.1, 24.7, 13.7, 11.1
***2° Trans* isomer 10c**: ^{1}H-NMR 0.82-1.10 (m, 8 H), 1.63 (m, 1 H), 3.67 (t, J=5.2), 5.23 (d, J=5.2), 6.42 (bs, 1 H), 7.25-7.45 (m, 5 H). ^{13}C-NMR 159.6, 139.4, 128.9, 128.8, 125.9, 125.8, 80.9, 64.9, 38.8 25.6,14.2, 11.4.
***1° Cis* isomer 11c**: ^{1}H-NMR 0.62-0.80 (m, 8 H), 1.49 (m, 1 H), 4.00 (dd, J=8.4, 5.7), 5.72 (d, J=8.4), 6.28, (bs, 1 H), 7.25-7.45 (m, 5 H). ^{13}C-NMR 160.3, 135.2, 128.7, 128.4, 127.1, 126.5, 81.3, 61.4, 34.8, 24.8, 14.3, 11.1
***2° Cis* isomer 11c**: ^{1}H-NMR 0.62-0.80 (m, 8 H), 1.49 (m, 1 H), 3.93 (t, J=8.1), 5.65 (d, J=8.1), 6.28 (bs, 1 H), 7.25-7.45 (m, 5 H). ^{13}C-NMR 160.4, 135.1, 128.7, 128.4, 127.1, 126.5, 81.6, 62.2, 34.5, 26.6, 15.5, 14.3, 11.4, 11.1

4,5-*trans*- and 4,5-*cis*-4-*t*-butyl-5-phenyl-1,3-oxazolidin-2-one 10d and 11d
(M^+, *Calcd* for $C_{13}H_{17}NO_2$: 219.1259, *Found* 219.1258), *m/e* 219 (M^+), 163, 118 (base-peak), 107, 91, 79, 77, 57. IR (nujol): 3220, 3140, 2980-2860, 1725, 1460, 1380, 1240.
***Trans* isomer 10d**: ^{1}H-NMR 0.99 (s, 9 H), 3.45 (d, 1 H J=3.8), 5.28 (d, 1 H J=3.8), 6.55 (bs, 1 H), 7.30-7.47 (m, 5 H). ^{13}C-NMR 159.4, 140.1, 128.9, 128.7, 125.6, 79.1, 69.3, 34.1, 24.9.
***Cis* isomer 11d**: ^{1}H-NMR 0.71 (s, 9 H), 3.85 (d, 1 H J=7.7), 5.73 (d, 1 H J=7.7), 6.17 (bs, 1 H), 7.30-7.47 (m, 5 H). ^{13}C-NMR 160.6, 135.3, 128.8, 128.3, 127.6, 81.8, 66.5 34.0, 26.1.

4,5-*trans*- and 4,5-*cis*-4-pentyl-5-phenyl-1,3-oxazolidin-2-one 10e and 11e
(M^+, *Calcd* for $C_{14}H_{19}NO_2$: 233.1416, *Found* 233.1418), *m/e* 233 (M^+), 162, 149, 118, 107 (base-peak), 91, 79, 43. IR (nujol): 3220, 3140, 2980-2860, 1725, 1460, 1380, 1240.
***Trans* isomer 10e**: ^{1}H-NMR 0.80-1.00 (m, 3 H), 1.22-1.47 (m, 6 H), 1.70 (m, 2 H), 3.72 (q, 1 H J=6.5), 5.11 (d, 1 H J=6.5), 6.57 (bs, 1 H), 7.25-7.50 (m 5 H). ^{13}C-NMR 159.3, 138.4, 128.8, 125.9, 83.7, 60.9, 34.9, 31.5, 25.1, 22.3, 13.9.
***Cis* isomer 11e**: ^{1}H-NMR 0.79-0.85 (m, 3 H), 1.22-1.47 (m, 6 H), 1.77 (m, 2 H), 4.03 (m, 1 H), 5.71 (d, 1 H J=8.2), 6.65 (bs, 1 H), 7.25-7.50 (m, 5 H). ^{13}C-NMR 160.3, 135.1, 128.4, 126.2, 81.1, 57.0, 31.4, 31.3, 25.1, 22.3, 13.9.

4,5-*trans*- and 4,5-*cis*-4-methyl-5-phenyl-1,3-oxazolidin-2-one 10f and 11f.

(M^+, *Calcd* for $C_{10}H_{11}NO_2$: 177.2028, *Found* 177.2027), *m/e* 177 (M^+) IR (nujol): 3220, 3140, 2980-2860, 1725, 1460, 1380, 1240.
***Trans* isomer 10f**: ^{1}H-NMR 1.39 (d, 3 H J=6.1), 3.84 (dq, 1 H J=7.4, 6.1), 5.04 (d, 1 H J=7.4), 6.22 (bs, 1 H), 7.30-7.52 (m, 5 H). ^{13}C-NMR 159.4, 137.9, 129.0, 126.0, 85.4, 56.4, 19.7.
***Cis* isomer 11f**: ^{1}H-NMR 0.81 (d, 3 H J=6.6), 4.21 (dq, 1 H J=8.0, 6.6), 5.71 (d, 1 H J=8.0), 6.12 (bs, 1 H), 7.30-7.52 (m , 5 H). ^{13}C-NMR 161.3, 135.1, 128.6, 125.8, 81.0, 52.3, 19.5.

4,5-*trans*- and 4,5-*cis*-4-allyl-5-methyl-1,3-oxazolidin-2-one 10g and 11g
(M^+-41, *Calcd* for $C_4H_6NO_2$: 100.0398, *Found* 100.0396), *m/e* 100(M^+-41), 82, 68, 56, 41. IR (nujol): 3300, 3080, 2980, 2940, 1740, 1640, 1390.
***Trans* isomer 10g**: ^{1}H-NMR 1.43 (d, 3 H J=6.3), 2.15-2.40 (m, 2 H), 3.48 (q, 1 H J=6.1), 4.35 (quintet, 1 H J=6.1), 5.15-5.25 (m, 2 H), 5.65-5.85 (m, 1 H), 5.98 (bs, 1 H). ^{13}C-NMR 159.7, 132.2, 118.8, 77.4, 58.4, 38.5, 19.6.
***Cis* isomer 11g**: ^{1}H-NMR: 1.39 (d, 3 H J=6.6),.2.15-2.40 (m, 2 H), 3.83 (m, 1 H), 4.82 (quintet, 1 H J=7.4), 5.15-5.25 (m, 2 H), 5.65-5.85 (m, 2 H). ^{13}C-NMR 159.7, 133.0, 118.6, 75.6, 54.6, 34.0, 14.2.

4,5-*trans*- and 4,5-*cis*-4-butyl-5-methyl-1,3-oxazolidin-2-one 10h and 11h
(M^+, *Calcd* for $C_8H_{15}NO_2$: 157.1103, *Found* 157.1106), *m/e* 157 (M^+),129, 100, 70, 56, 43, 41. IR (nujol): 3220, 3140, 2980-2860, 1725, 1460
***Trans* isomer 10h**: ^{1}H-NMR 0.90 (m, 3 H), 1.20-1.37 (m, 4 H), 1.40 (d, 3 H J=6.3), 1.40-1.60 (m, 2 H), 3.39 (q, 1 H J=6.3), 4.28 (quintet, 1 H J=6.3), 6.50 (bs, 1 H). ^{13}C-NMR 159.9, 79.0, 59.7, 34.4, 27.2, 22.2, 20.0, 13.5.
***Cis* isomer 11h**: ^{1}H-NMR 0.90 (m, 3 H) 1.20-1.37 (m, 4 H), 1.33 (d, 3 H J=6.7), 1.40-1.60 (m, 2 H), 3.75 (q, 1 H J=7.0), 4.76 (quintet, 1 H J=7.0), 6.50 (bs 1 H). ^{13}C-NMR 160.2, 76.2, 55.7, 29.3, 28.0, 22.3, 14.5, 13.5.

4,5-*trans*- and 4,5-*cis*-4-*t*-butyl-5-methyl-1,3-oxazolidin-2-one 10i and 11i
(M^+, *Calcd* for $C_8H_{15}NO_2$: 157.1103, *Found* 157.1105), *m/e* 157 (M^+), 101 (base-peak), 100, 99, 71, 70, 57, 56, 41. IR (nujol): 3220, 3140, 2980-2860, 1725, 1460, 1380, 1240.
***Trans* isomer 10i**: ^{1}H-NMR 0.90 (s, 9 H), 1.41 (d, 3 H J=6.3), 3.09 (d, 1 H J=4.6), 4.46 (dq, 1 H J=6.3, 4.6), 6.40 (m, 1 H). ^{13}C-NMR 160.0, 74.6, 68.6, 33.2, 24.6, 22.0,
***Cis* isomer 11i**: ^{1}H-NMR 1.02 (s, 9 H), 1.52 (d, 3 H J=7.0), 3.50 (d, 1 H J=7.0), 4.79 (quintet, 1 H J=7.0), 5.70 (m 1 H). ^{13}C-NMR 160.0,.77.7, 16.3, 64.9, 33.5, 26.4

4,5-*trans*- and 4,5-*cis*-4-cyclopropyl-5-methyl-1,3-oxazolidin-2-one 10j and 11j
(M^+, *Calcd* for $C_7H_{11}NO_2$: 141.0790, *Found* 141.0788), *m/e* 141 (M^+), 113, 97, 70, 69, 68 (base-peak), 56, 43. IR (nujol): 3220, 3140, 2980-2860, 1725, 1460, 1380, 1240.
***Trans* isomer 10j**: ^{1}H-NMR 0.20-0.32 (m, 2 H), 0.51-0.65 (m, 2 H), 0.82-0.98 (m, 1 H), 1.43 (d, 3 H J=6.3), 2.79 (dd, 1 H J=7.5, 6.3), 4.49 (quintet, 1 H J=6.3), 6.24 (bs, 1 H). ^{13}C-NMR 159.2, 79.3, 64.6, 20.2, 14.3, 2.1, 1.5.
***Cis* isomer 11j**: ^{1}H-NMR 0.15-0.25 (m, 2 H), 0.55-0.62 (m, 2 H), 0.82-0.98 (m, 1 H), 1.50 (d, 3 H J=6.6), 3.03 (dd, 1 H J=9.1, 7.9), 4.79 (quintet, 1 H J=6.6), 6.24 (bs, 1 H). ^{13}C-NMR 159.2, 76.3, 61.4, 15.5, 10.8, 2.5, 2.4

4,5-*trans*- and 4,5-*cis*-4-allyl-5-crotyl-1,3-oxazolidin-2-one 10k and 11k
(M^+-41, *Calcd* for $C_6H_8NO_2$: 126.0555, *Found* 126.0557), *m/e* 126(M^+-41) (base-peak), 82, 71, 67, 55, 41. IR (nujol): 3220, 3140, 2980-2860, 1725, 1460, 1380, 1240

***Trans* isomer 10k**: ^{1}H-NMR 1.75 (dd, 3 H J=6.3, 1.2), 2.30 (m, 2 H), 3.58 (m, 1 H), 4.56 (dd, 1 H J=7.0, 7.1), 5.10-5.22 (m, 2 H), 5.54 (m, 1 H), 5.65-5.75 (m, 1 H), 5.85 (m, 1 H), 6.02 (bs, 1 H). ^{13}C-NMR 158.9, 132.3, 132.2, 127.1, 119.3, 82.6, 57.6, 38.5, 17.7.
***Cis* isomer 11k**: ^{1}H-NMR 1.77 (dd, 3 H J=6.6, 1.2), 2.30 (m, 2 H), 3.83 (m, 1 H), 5.04 (dd, 1 H J=7.8, 7.9), 5.10-5.22 (m, 2 H), 5.54 (m, 1 H), 5.65-5.75 (m, 1 H), 5.85 (m, 1 H), 6.02 (bs 1 H). ^{13}C-NMR 159.6, 133.1, 133.1, 123.7, 119.3, 80.4, 55.3, 35.7, 17.8.

4,5-*trans*- and 4,5-*cis*-4-*i*-butyl-5-crotyl-1,3-oxazolidin-2-one 10l and 11l
(M^+, *Calcd* for $C_{10}H_{17}NO_2$: 183.1259, *Found* 183.1256), *m/e* 183 (M^+), 126, 113, 82, 71 (base-peak), 55, 43. IR (nujol): 3220, 3140, 2980-2860, 1725, 1460, 1380, 1240
***Trans* isomer 10l**: ^{1}H-NMR 0.91 (d, 3 H J=6.8), 0.93 (d, 3 H J=6.8), 1.30-1.73 (m, 3 H), 1.75 (dd, 3 H J=6.6, 1.1), 3.57 (m, 1 H), 4.46 (dd, 1 H J=7.4, 7.5), 5.54 (m, 1 H), 5.86 (m, 1 H), 6.15 (bs 1 H). ^{13}C-NMR 159.4, 132.1, 127.3, 83.9, 56.7, 43.5, 25.0, 23.0, 21.9 17.7.
***Cis* isomer 11l**: ^{1}H-NMR 0.90 (d, 3 H J=6.8), 0.94 (d, 3 H J=6.8), 1.30-1.73 (m, 3 H), 1.77 (dd, 3 H J=6.6, 1.1), 3.90 (ddd, 1 H J=10.5, 8.2, 4.0), 4.99 (dd 1 H J=8.2, 8.1), 5.54 (m, 1 H), 5.86 (m, 1 H), 6.10 (bs, 1 H). ^{13}C-NMR 159.5, 132.7, 124.1, 81.1, 54.1, 39.6, 24.9, 23.5, 21.3, 17.8.

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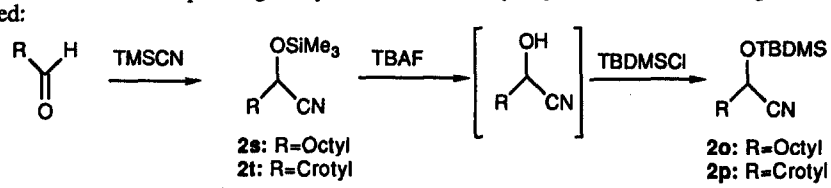
24 Commercially available lactonitrile and mandelonitrile were used. Cyanohydrins **1b**, **1o** and **1p** were prepared from the corresponding aldeyde *via* the trimethylsilylderivative according the scheme below reported:



2s: R=Octyl
2t: R=Crotyl

2o: R=Octyl
2p: R=Crotyl

The trityl protected cyanohydrins were prepared as described in the experimental section.

25 The relative stereochemistry of the new C-3 chiral center with reference to the other two (C-2 and C-1) was not determined. However a 1:1 mixture of C-3 isomers were obtained either in the case of the *syn* isomer as in the case of *anti* one.

26 The relative configurations of the aminols protected on the hydroxy functionality as methyl or trityl ethers were deduced directly from the relative spectra by comparison with the spectra of the corresponding silyl derivatives in which the configuration was been assigned by elaboration to the oxazolidin-2-ones.

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