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Stereocontrolled Synthesis of Chiral Secondary (α-methylene-β-Substituted)-γ-Lactams by Addition of β-Functional Crotylzinc Reagents to Chiral Imines.

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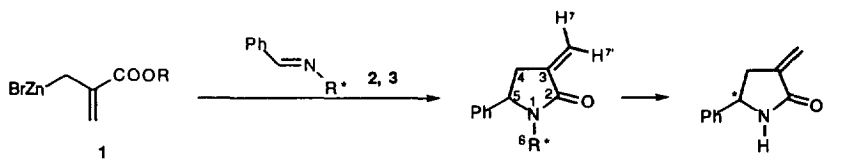
Abstract : Stereocontrolled addition of functionalised crotylzinc reagents to chiral imines derived either from N-α-aminoesters or N-β-aminoalcohols furnished secondary α-methylene-β-substituted-γ-lactams in excellent diastereoisomeric excess (de ≈ 92-100%).

Continuing our interest in the development of new methods useful in the construction of secondary α-methylene-γ-lactams **6**, we have recently reported that the stereocontrolled addition of organozinc reagent **1** to chiral imines derived either from N-α-aminoesters **2** or N-β-aminoalcohols **3** as chiral auxiliaries proceeds in good yields and with high enantiomeric excess (ee > 95%) [1,2].



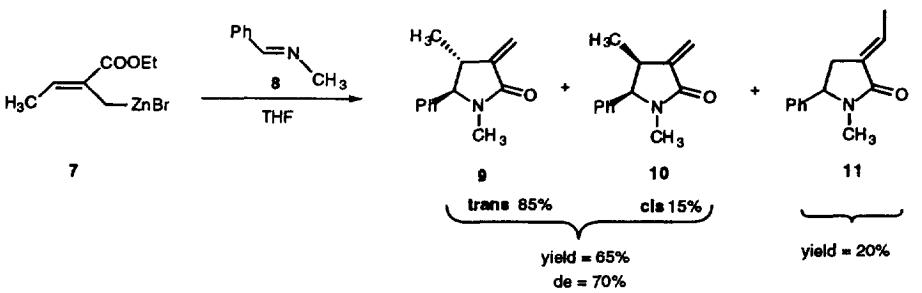
1 — **1a** R = Et, **1b** R = tBu; **4,5**; **6a, b** — **a** : 5R, **b** : 5S

allylzinc	Imine (R)	Lactams
1 a	**2a** : -CH(Ph)COOEt (R)	**4 a** 5-(R) 6-(R)
1 a	**2b** : -CH(Ph)COOEt (S)	**4 b** 5-(S) 6-(S)
1 b	**3a** : -CH(Ph)CH_2OH (R)	**5 a** 5-(R) 6-(R)
1 b	**3b** : -CH(Ph)CH_2OH (S)	**5 b** 5-(S) 6-(S)

The mechanism we have proposed to explain the high degree of enantioselectivity involves a chair like transition state including metal chelation by the ester function or hydroxyl group of the imines **2**, **3** and allylic transposition.

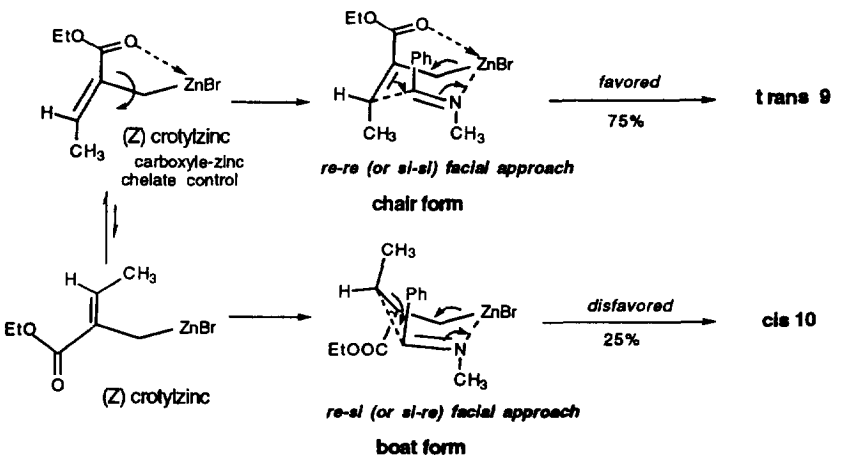
In connection with mechanistic investigations and optimisation of the above mentioned reaction, we wish to report here our results on the stereocontrolled addition of organozinc reagents derived from homologues of (α-bromomethyl)acrylates to chiral imines. In our preliminary study, we decided to use crotylzinc **7** derived from ethyl 2-(bromomethyl)but-2-enoate as a model compound and first examine its reaction with an achiral imine **8** (N-benzylidenemethylamine).

The isolated organozinc reagent **7** (1.0 to 1.1eq) prepared via the literature method [3,4], was slowly added to a THF solution of **8** (1 eq) and the temperature controlled between 20-30°C. Under these conditions, we observed the formation of N-methyl-(α-methylene-β-methyl-γ-phenyl)-γ-butyrolactams **9** and **10** resulting of a coupling with allylic transposition and cyclization sequence in a 85/15 ratio of *trans /cis* products according to the ^{1}H NMR spectrum analysis (yield = 65%).



As a side product we also isolated **11** in 20% yield from a mechanism proceeding without allylic transposition as described in the literature [5,6]. Under usual experimental conditions (0-20°C, 0-1h) and with unhindered reaction partners, the branched isomer is strongly preferred. The formation of the alkylidene product is often rationalised by the assumption that the addition of allylic organozinc reagents to aldehydes, ketones and imines is reversible. However, in our case reversibility is strongly concurrenced by the cyclization step.

The *trans* selective formation of **9** can be explained by considering a closed transition state (chair form) involving a (Z) crotylzinc and the preferred (*E*) aldimine geometry [7,8]. In the *re-re* (or *si-si*) facial approach, the organozinc methyl substituent occupies a pseudo axial position and the imine carbon-substituent is forced into a pseudo axial position by coordination of nitrogen lone pair to the metal .

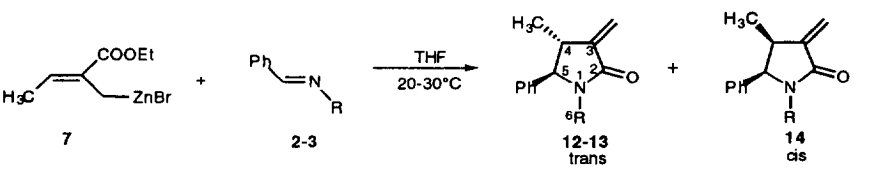


In contrast, the minor product **10** (*cis* product) results from a ***re-si (or si-re)*** facial approach (rotation around the carbon-carbon bond of the C=C-CH_2ZnBr moiety) and probably involves a boat like transition state. This transition state is highly speculative, even if steric interactions between organozinc methyl substituent, ester function and the imine phenyl group are not clearly rationalized. Contamination by the participation of ***(E)*** crotylzinc reagent (resulting from an isomerisation process of allylic organozinc reagent [3,4]) in a chair like transition state is improbable in view of recent studies in our laboratory.

In light of this, we investigated the reaction of the crotylzinc reagent **7** with chiral imines bearing a subtituent able to chelate the metal. Our hypothesis was that such a chelation control should dramatically improve the regio and stereoselectivity of this reaction.

As expected, we found that reaction of **7** (1eq) with chiral imines **2a-b** (1eq) gave the **unique *trans*-form** of the corresponding (α-methylene-β-methyl-γ-phenyl)-γ-lactams **12a-b** in good selectivity (de = 100%, ee = 92%) and satisfactory isolated yields (86%).

In the case of the chiral imines **3a-b** (1eq), two equivalents of **7** are required to complete lactamisation. Meanwhile, the yield of the corresponding (α-methylene-β-methyl-γ-phenyl)-γ- lactams **13a-b** was lower (60%) and the diastereoselectivity less pronounced (de = 92%)

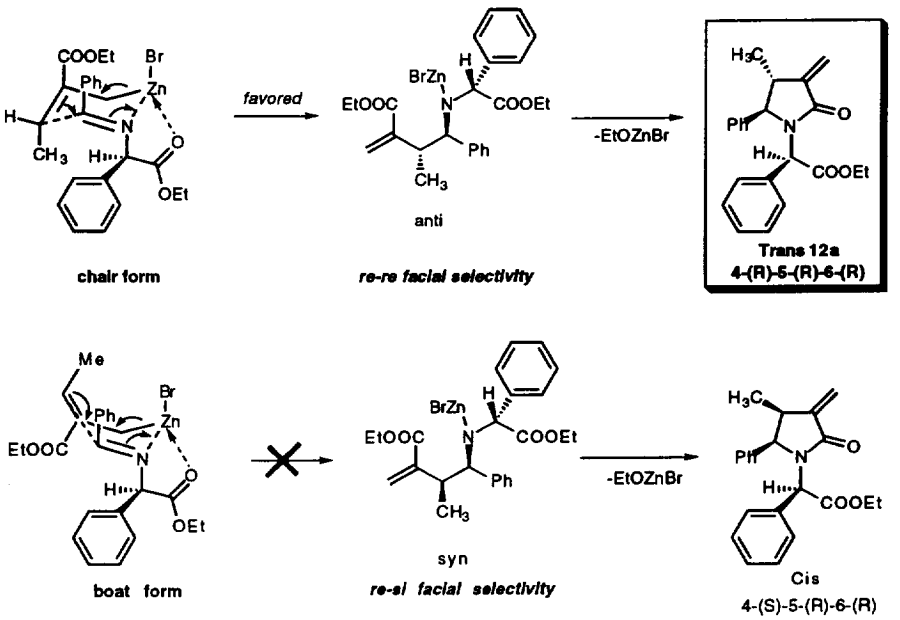


Crotylzinc 7	Imine (R)	Lactam	de (%)	yield(%)
(1 eq)	**2a** : -CH(Ph)COOEt (R)	**12a** 4-(R) 5-(R) 6-(R)	100	86
(1 eq)	**2b** : -CH(Ph)COOEt (S)	**12b** 4-(S) 5-(S) 6-(S)	100	86
(2 eq)	**3a** : -CH(Ph)CH_2OH (R)	**13a** 4-(R) 5-(R) 6-(R) **+14**	92	60
(2 eq)	**3b** : -CH(Ph)CH_2OH (S)	**13b** 4-(S) 5-(S) 6-(S) **+14**	92	60

The remarkable complete stereocontrol at two stereogenic centers in lactam **12** may be interpreted by evoking that crotylzinc addition to chiral imine **2**, bearing substituents capable of chelating the metal, proceeds through the compact cyclic chair transition state **A** in which the maximum stabilisation is attained [9]. According to such a model, chelation control forces the crotyl metal moiety to react exclusively via its ***re face*** from **a (R) imine** resulting in a **total *trans* selectivity**. As a consequence, no side product as **11** and no *cis* lactam allowing to proceed from cyclic boat transition state **B** which would involved a ***si facial addition*** of the crotylmetal was detected.

On the other hand, although the details of the mechanism are still not clear, the slightly lower diastereoselectivity obtained with chiral imine **3** can be rationalized by the assumption that addition of two

equivalents of crotylzinc **7** to one equivalent of **3** might affect the chelation controlled mechanism and the chair like transition state described above.

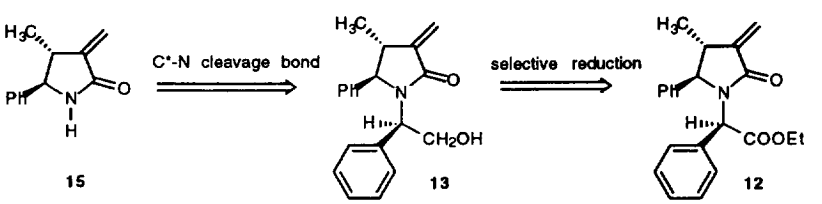


Synthesis of *trans* secondary (α-methylene-β-methyl-γ-phenyl)-γ- lactam **15** by selective removal of the chiral auxiliary from lactams **12** and **13** has been performed taking in account that :

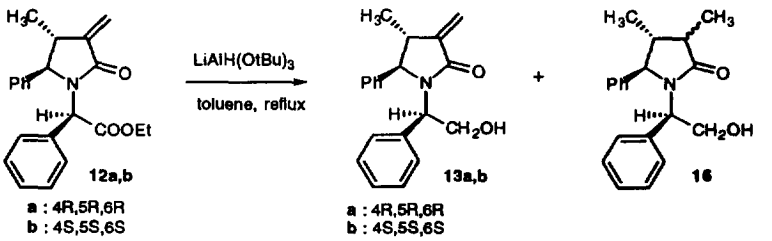
i) as we reported in a recent paper [2], removal of chiral auxiliary exclusively can be realised starting from iminoalcohol **3**,

ii) stereocontrolled addition of isolated crotylzinc **7** to chiral imine **2** proceeds with exceptional and higher selectivity (de = 100%, yield = 86%) than with chiral imine **3** (de = 92%, yield = 60%)

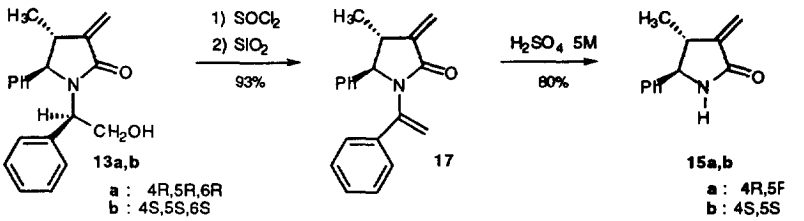
We planned to synthesise **15** following the retrosynthetic scheme :



Lactam **12** obtained by our diastereoselective method, was reduced with excellent chemoselectivity using lithium terbutoxyaluminium hydride. It affords 60% yield of *trans* lactam **13**. It is worth noting that either prolonged reaction time or increased reducing agent molarity led to by-product **16**.



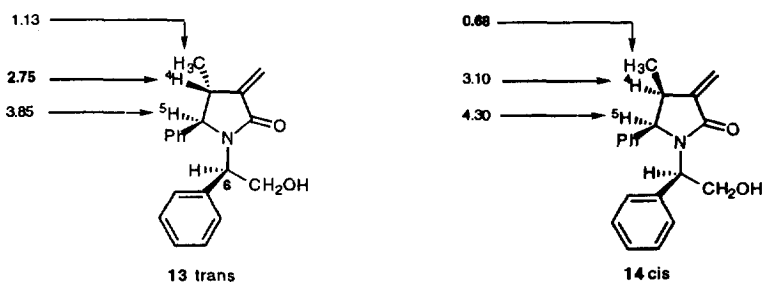
Finally, reaction of **13** with thionyl chloride followed by elimination of hydrochloric acid on silica gel led to the enamide **17** which was then hydrolysed with 5M aqueous sulphuric acid to give **15** (de = 100%, overall yield 75%).



Determination of diastereoisomeric purity

**Cis / Trans Ratios :*

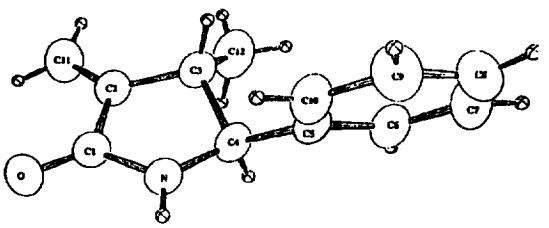
The Cis/Trans ratio of **13** has been determined via the observed and integrated signals for H^4, H^5 and CH_3-4 obtained from classical and Noesy N.M.R. experiments. We were able to observe that in trans diastereoisomer **13**, H^4 must be shielded by the phenyl group (δ(ppm) = 2.75) and H^5 must be shielded by the methyl group (δ(ppm) = 3.85). In contrast, methyl protons signals of the *trans* diastereoisomer **13** appear further downfield (δ(ppm) = 1.13) than those of the cis diastereoisomer **14** (δ(ppm) = 0.68) as shown below.



** Enantiomeric excess (RR,SS)*

The enantiomeric purity of lactams **12** and **13** were determined from ^1H N.M.R. spectra ($CDCl_3$ as solvent) by using the $Eu(hfc)_3$. The absolute configurations of trans lactams **12** and **13** were tentatively assigned as 4R,5R,6R or 4S,5S,6S depending on the chiral auxiliary used. HPLC analysis of **12a** and **12b** on a chiral stationary phase revealed only one peak for each diastereoisomer.

After deprotection of lactam **13** a crystal of pure lactam **15** was submitted to an X-ray diffraction study. The analysis confirmed the presence of a single diastereoisomer and allowed us to assign to C3 and C4 stereocenters the trans configuration.



ORTEP Diagram of trans lactam 15 $C_{12}H_{13}NO$

The stereochemistry has been determined by a single crystal X-ray analysis. Crystal data : $C_{12}H_{13}NO$, M = 187.24, orthorhombic, group space $P2_1P2_1P2_1$, a = 8.122(9), b = 10.457(4), c = 12.145(5) Å, V = 1032(2)Å^3. Z = 4, ρ calc = 1.206 g/cm^{-3}, F(000) = 400. Monochromated Mo-Kα radiation m = 0.71 cm-1. R = 0.033 for 790 reflexions with I>3σ(I).

In conclusion, very high 1,3 asymmetric induction extended to a 1,4 stereocontrol is realized via the reaction of β–functionalised crotylzinc with chiral imines bearing nitrogen substituant able to chelate the metal. A mechanism is proposed to explain the **high regio and diastereoselectivity** of this reaction. The present development provides an excellent method for synthesis of various secondary (β,γ substituted) α-methylene-γ-lactams with good yields and **simultaneous complete or quasi complete stereocontrol of two adjacent stereogenic centers (ee > 92%)**.

EXPERIMENTAL

Apparatus : ^{1}H and ^{13}C NMR spectra were recorded with Bruker AC 200 and Bruker AMX 400 spectrometers in chloroform-d_1, chemical shifts are expressed in ppm. IR spectra were recorded on a Perkin-Elmer 1420 infrared spectrophotometer. Mass spectra (m/z (% base peak)) were recorded on a HP 5889A spectrometer EI (70 eV). For high performance liquid chromatography (H.P.L.C.) analysis a Hewlett Packard model (HP 1050) equipped with a UV detector (254 nm) and a CHIRACEL OD-H column was employed. Optical rotations were measured on a AA.10 OPTICAL ACTIVITY polarimeter. Melting points were determined on C. REICHERT microscope apparatus and are uncorrected. Elemental analyses were carried out on a Perkin-Elmer 2400 C, H, N elemental analyser. For X-ray analysis : Atomic scattering factors from International Tables for X-ray Crystallography [10]. The calculations were performed on a Hewlett Packard 9000-710 for structure determination [11] and on a Digital MicroVAX 3100 computer with the MOLEN package [12] for refinement and Ortep calculations.

Chemicals : Tetrahydrofuran (THF) was prepared by pre-drying with KOH followed by distillation from Na/benzophenone, diethyl ether was distilled from Na/benzophenone, dichloromethane, ethyl acetate, were dried

by the distillation over P_2O_5. Hexane were dried by the distillation over $CaCl_2$ and toluene were distilled from sodium. N-β-aminoalcohols, N-α-aminoesters, chiral iminoesters and iminoalcohols were prepared according to classical procedures [13].

Preparation of crotylzinc **7** :

In a typical experiment, a dry four necked round bottom flask with a mechanical stirrer, a thermometer and nitrogen inlet was charged with zinc granular 30 mesh pre-activating by washing with hydrochloric acid 2N (1g 0.15 at.gr)(JANSSEN). Then a drop of pure ethyl 2-(bromomethyl)but-2-enoate was added in order to start the reaction (reaction temperature rises and must be cooled to 17°C). To the resulting mixture, a solution of ethyl 2-(bromomethyl)but-2-enoate (2.07g, 10 mmol) in THF (10 ml) was slowly added and the reaction was stirred at 17-20°C until no more starting material was detected by GC.

General procedure for the preparation of α-methylene γ-lactams

1-methyl-3-methylene-4-methyl-5-phenyl-pyrrolidinone **9, 10** :

To a solution of N-benzylidenemethylamine **8** (10 mmol) in THF (50 ml) was added the precedent solution of crotylzinc **7** (10 mmol) and after stirring for 6h at room temperature, the reaction mixture was hydrolysed at - 20°C with a saturated NH_4Cl solution and extracted with ethyl acetate (3x30 ml). The combined layers were dried ($MgSO_4$) concentrated and the crude product purified by column chromatography on silica gel (hexane/ethyl acetate : 70/30) to afford **9** as white crystals, **10** and **11** (85%).

Trans isomer **9** : mp 49°C; ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.26 (d, 3H, J=7.0, CH_3), 2.71 (m, 1H, H^4), 2.74 (s, 3H, N-CH_3), 3.96 (d, 1H, J=5.1, H^5), 5.29 (d, 1H, J=2.4, $H^{7'}$), 6.07 (d, 1H, J=2.8, H^7), 7.3 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ: 17.7 (CH_3), 28.5 (N-CH_3), 40.0 (CH^4), 70.2 (CH^5), 114.4 (C=CH_2), 126.6, 128.2, 129.0, 139.8 (Ph), 144.8 (C=CH_2), 168.4 (C=O).

Cis isomer **10** : ^1H NMR ($CDCl_3$, 200 MHz) δ: 0.75 (d, 3H, J=7.1, CH_3), 2.82 (s, 3H, N-CH_3), 3.28 (m, 1H, H^4), 4.60 (d, 1H, J=8.3, H^5), 5.22 (d, 1H, J=2.9, $H^{7'}$), 6.07 (d, 1H, J=3.1, H^7), 7.0 (m, 2H, Ph), 7.3 (m, 3H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ: 14.2 (CH_3), 28.8 (N-CH_3), 36.5 (CH^4), 66.5 (CH^5), 114.5 (C=CH_2), 128.0, 128.5, 129.0, 139.9 (Ph), 144.6 (C=CH_2), 168.7 (C=O).

Ethylidene lactame **11** : 1.75 (dt, 3H, J=7.1, J=1.8, CH_3), 2.5 (m, 1H, $H^{4'}$), 2.74 (s, 3H, N-CH_3), 3.13 (m, 1H, H^4), 4.51 (dd, 1H, J=4.1, J=8.7, H^5), 6.59 (qt, 1H, J=7.1, J=2.8, H^7), 7.0 (m, 2H, Ph), 7.3 (m, 3H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 14.5 (CH_3), 28.4 (N-CH_3), 32.6 (CH_2), 61.6 (CH^5), 126.2 (CH^7), 127.8, 128.0, 129.0, 131.4 (Ph), 141.5 (C=CH^7), 168.7 (C=O). IR 2960, 1690, 1660 cm^{-1}; EI-MS : 201 (M^+, 100) 124 (69), 118 (22), 82 (22), 54 (39), 28 (22). Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96 Found : C, 77.55; H, 7.17; N, 6.81.

Ethyl [3-methylene-4-methyl-5-phenylpyrrolidinone-1-yl]-2-phenylacetate **12** : was obtained using the same procedure in 86% yield (White crystalline solid).

Trans isomer **12a,b** : ^1H NMR ($CDCl_3$, 200 MHz) δ: 1.17 (d, 3H, J=6.9, CH_3CH), 1.19 (t, 3H, J=7.2, CH_3CH_2), 2.78 (m, 1H, H^4), 3.98 (d, 1H, J=5.5, H^5), 4.10 (q, 2H, J=7.2, CH_3CH_2), 5.24 (s, 1H, H^6), 5.34 (dd, 1H, J=0.4, J=2.3, $H^{7'}$), 6.13 (dd, 1H, J=0.4, J=2.7, H^7), 7.2 (m, 10H, Ph) ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ : 14.1 (CH_3CH_2), 17.4 (CH_3CH), 42.8 (CH^4) 60.9 (CH^5), 61.5 (CH_2CH_3), 69.5 (CH^6), 115.6 (C=CH_2), 127.8, 127.9, 128.0, 128.2, 128.3, 129.8, 134.0, 139.6 (Ph), 144.3 (C=CH_2), 168.9 (C=O lactam), 169.0 (C=O ester). IR : 2980, 1730, 1685, 1650 cm^{-1}; EI-MS : 349 (M^+, 3), 276 (100), 171 (11), 143(15), 128 (16), 106 (9), 91 (9). Anal. Calcd. for $C_{22}H_{23}NO_3$: C, 75.62; H, 6.63; N, 4.01 Found : C, 75.57; H, 7.11; N, 4.06.

12a (4R,5R,6R) : $[\alpha]_D^{25}$ = -27 (c 1.8, $CHCl_3$); mp 75°C. **12b** (4S,5S,6S) : $[\alpha]_D^{25}$ = +28 (c 1.3, $CHCl_3$); mp 84°C

[3-methylene-4-methyl-5-phenylpyrrolidinone-1-yl]-2-phenylethanol **13** :

To a solution of N-benzylidene-α-phenylglycinol (2.25g, 10 mmol) in THF (50 ml) was added **7** (20 mmol) prepared according to the procedure described above. After stirring one night , the reaction was hydrolysed at - 20°C with a saturated NH_4Cl solution and finally extracted with ethyl acetate (3 x 30 ml). The combined layers were dried ($MgSO_4$) concentrated and the crude product purified by column chromatography on silica gel (hexane/ethyl acetate : 60/40) to afford **13** as white crystals (56%).

Trans isomer **13a,b** : ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.13 (d, 3H, J=6.9, CH_3), 2.75 (m, 1H, H^4), 2.88 (bs, 1H, OH), 3.77 (dd, 1H, J=-11, J=5.6, CH_2OH), 3.85 (d, 1H, J=4.4, H^5), 3.93 (dd, 1H, J=-11, J=8.5, CH_2OH), 5.05 (dd, 1H, J=5.6, J=8.5, H^6), 5.38 (d, 1H, J=2.1, $H^{7'}$), 6.16 (d, 1H, J=2.5, H^7), 7.2 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ : 18.6 (CH_3), 42.3 (CH^4), 60.6 (CH^5), 63.0 ($\underline{C}H_2OH$), 69.0 (CH^6), 115.8 (C=$\underline{C}H_2$), 127.2, 127.8, 128.3, 128.4, 128.5, 136.4, 140;5 (Ph), 145.0 ($\underline{C}$=CH_2), 169.7 (C=O). IR : 3330, 2980, 1670, 1640 cm^{-1}; EI-MS : 308 (M+1) (1), 276 (100), 186 (5) 171 (13) 143 (19) 128 (17) 106 (10) 91 (11) 77 (7). Anal. Calcd. for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56 Found : C, 77.98; H, 7.05; N, 4.48. **13a** (4R,5R,6R) : $[\alpha]_D^{25}$ = +34.5 (c 1.2, $CHCl_3$); mp 117°C. **13b** (4S,5S,6S) : $[\alpha]_D^{25}$ = -35 (c 1.2, $CHCl_3$); mp 114°C.

Procedure for reduction of ***12*** *with terbutoxyalumunium hydride :*

To a solution of lactam **12** (700 mg, 2 mmol) in toluene (20 ml) was slowly added lithium terbutoxyaluminium hydride (765 mg, 3 mmol) and the resulting mixture was stirred at reflux of the solvent for 30 min. The reaction mixture was then hydrolysed with a 1M solution of HCl (20 ml), extracted with ethyl acetate (3 x 30 ml) and washed with brine (20 ml). After drying ($MgSO_4$) and solvent evaporation, a silica gel chromatography (hexane/ethyl acetate : 50 /50) of the residue provided the lactam **13** as a white crystalline solid (60%) with ^1H NMR identical with the sample prepared above.

General procedure for removal of chiral auxiliary

[3-methylene-4-methyl-5-phenylpyrrolidinone-1-yl]-2-phenylethylene **17** :

To a solution of **13** (460 mg, 1.5 mmol) in THF (30ml) was added, at 0°C, $SOCl_2$ (0.22 ml, 3 mmol). The resulting mixture was stirring for 15 min at 0°C then 30 min at reflux of solvent. After evaporation of the solvent, the crude product was washed with a saturated $NaHCO_3$ solution and extracted with ethyl acetate (3 x 40 ml). After drying ($MgSO_4$) and solvent evaporation, a silica gel chromatography (hexane/ethyl acetate : 80 /20) of the residue provided the lactam **17** as a white crystalline solid (93%).

Trans isomer **17** : ^1H NMR ($CDCl_3$, 200 MHz) δ : 1.29 (d, 3H, J=7.0, CH_3), 2.86 (m, 1H, H^4), 4.25 (d, 1H, J=5.2, H^5), 5.20-5.29 (2s, 2H, CH_2 meth), 5.42 (dd, 1H, J=0.5, J=2.6, $H^{7'}$), 6,21 (dd, 1H, J=0.5, J=2.4 , H^7), 7.00-7.30 (m, 10H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ : 17.8 (CH_3), 41.7 (CH^4), 68.6 (CH^5), 112.1 (C_6H_5-C=$\underline{C}H_2$), 116.3 (CH-C=$\underline{C}H_2$), 126.8, 127.2, 127.9, 128.2, 128.4, 128.5, 136,2, 139,7 (Ph), 142.0 (C_6H_5-$\underline{C}$=CH_2), 144.8 (CH^4-$\underline{C}$=CH_2), 167;4 (C=O). IR : 1700, 1660, 1455-1445 cm^{-1}; EI-MS : 289 (M^+, 100), 288 (37), 260 (7), 198 (10), 170 (64), 128(22), 103 (28), 77 (34), 54 (27); **17a** (4R,5R) : $[\alpha]_D^{22}$ = +136 (c 0.5, $CHCl_3$); mp 47°C. **17b** (4S,5S) : $[\alpha]_D^{22}$ = -135 (c 1.1, $CHCl_3$); mp 45°C.

3-methylene-4-methyl-5-phenylpyrrolidinone **15** :

To a solution of **17** (145 mg, 0.5 mmol) in ether (20 ml) was added 5 ml of an aqueous solution of H_2SO_4 (5M). Then the resulting mixture was stirred at reflux of solvent until no more starting material was observed by TLC monitoring. The reaction mixture was washed with a saturated $NaHCO_3$ solution (20 ml), extracted with

ethyl acetate and the combined layers washed with brine prior to drying ($MgSO_4$) and solvent evaporating. Silica gel chromatography of the residue provided lactam **15** as white crystals (80%).

Trans isomer **15** : ^1H NMR ($CDCl_3$, 200 MHz) δ : 1.29 (d, 3H, J=6.9, CH_3), 2.77 (m, 1H, H^4), 4.19 (d, 1H, J=5.8, H^5), 5.32 (dd, 1H, J=0.6, J=2.6, $H^{7'}$), 6.06 (d, 1H, J=3.0, H^7), 6.42 (bs, 1H, NH), 7.3-7.4 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ : 16.8 (CH_3), 44.3 (CH^4), 63.6 (CH^5), 115.4 (C=CH_2), 126.1, 128.3, 128.9, 141.2 (Ph), 144.8 (C=CH_2), 170.3 (C=0). IR : 3190, 1700, 1660 cm^{-1}; EI-MS : 187 (M^+, 100), 158 (10), 143 (8), 106 (12), 104 (19), 82 (53), 77 (15), 54 (78) Anal. Calcd. for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48 Found : C, 77.18; H, 6.52; N, 7.25. **15a** (4R,5R) : $[\alpha]_D^{24}$ = +16 (c 0.5, $CHCl_3$); mp 146°C. **15b** (4S,5S) :$[\alpha]_D^{24}$ = -17 (c 0.6, CHCl3); mp 142°C.

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