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Efficient Synthesis of *syn*-Aziridino Alcohols by Chelation-Controlled Addition of Dialkylzincs and Grignard Reagents to N-Benzylaziridino Aldehydes

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Abstract: N-Benzyl aziridino aldehydes, derived from (L)-serine and (L)-threonine react with dialkylzinc and alkylmagnesium halides leading to *syn*-aziridino alcohols as single or major stereoisomers. The diastereoselectivity is affected by the nature of the organometallic and the solvent system.

Keywords: Diastereoselective synthesis, aziridines, aminoalcohols, alkylzincs, aminoaldehydes

The diastereoselective addition of organometallics to α-amino aldehydes has been well studied[1] and frequently applied to the synthesis of biologically important β-amino alcohols. Additions of alkylmetals to aziridino aldehydes to obtain aziridino alcohols have been less investigated, and have revealed moderate to good diastereoselectivities with *syn* adducts always predominating.[2] These aziridino alcohols have been recently tested as promoters for the enantioselective additions of dialkylzincs to N-(diphenylphosphinoyl)imines[3] and aldehydes,[4] and as starting materials for the synthesis of enantiopure α-aminoacids.[5]

On the contrary, the addition of alkyl metals to α,β-epoxy aldehydes have been applied many times to the synthesis of products having three consecutive stereogenic centers as intermediates for natural products.[6] The reactions occur with moderate to good stereoselection leading to *anti*[7] or *syn* [6] adducts as major diastereoisomers depending on the alkyl metals used.

Organozinc reagents have been scarcely used in diastereoselective additions to chiral amino aldehydes. Recently, we have reported the synthesis of enantiopure *syn*-β-amino alcohols by chelation-controlled additions of diethylzinc to α-(dibenzylamino)aldehydes.[8] On the basis of this work we decided to explore the diastereoselective alkylation of (S)-aziridine-2-carboxaldehyde **1a** and (2S, 3S)-3-methyl-2-formylaziridine **1b**, synthetic equivalents of (L)-serinal and (L)-threoninal respectively.

Starting aziridinoaldehydes **1a-b** were prepared by Swern oxidation[9] of the corresponding aziridino alcohols obtained in two steps from (L)-methyl serinate and (L)-methyl threoninate respectively.[3b]

The reaction of **1a-b** with dialkylzincs or alkylmagnesiun halides yielded a mixture of *syn*- and *anti*-aziridino alcohols in moderate chemical yields and good to excellent diastereomeric excesses (Scheme 1), and the reaction conditions were initially tested on the additions to **1a** (entries 1-5 in Table 1). The reaction of

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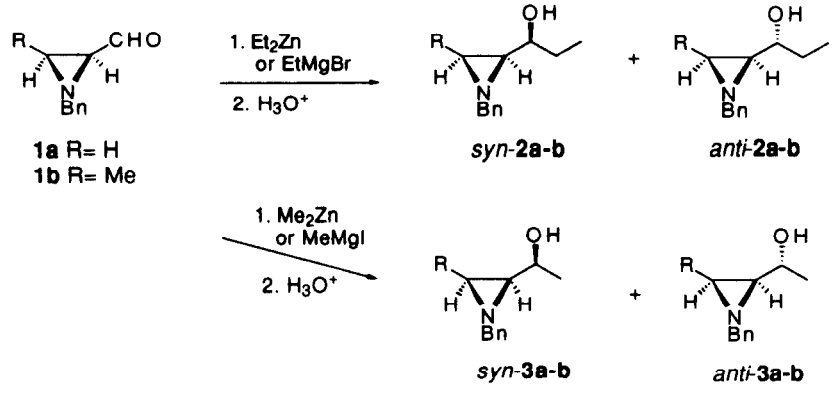
aziridino aldehyde **1a** with two equivalents of Et_2Zn or EtMgBr (1.2 equiv.) afforded a mixture of ethylated derivatives where the *syn*-diastereoisomer always predominates.

The *syn*-selectivity depends on the reaction conditions as can be seen in Table 1. A mixture of toluene-hexane is the preferred solvent for the reaction with Et_2Zn, whereas diethyl ether is the solvent of choice for the reaction with EtMgBr. The use of THF in the last reaction decreased the d.e. to 30% (entry 4), and the presence of an additive with strong coordination character such as TMEDA lead to a near equimolar mixture of *syn*- and *anti*-**2a** (entry 5).The temperature does not apreciably modify the stereochemical results. Indeed, Et_2Zn provides a much better diastereoselection than does EtMgBr, but similar results were obtained in the reactions of **1a** with Me_2Zn or MeMgI (compare entries 6 and 7).



Scheme 1

It is interesting to note that, contrary to previously described for N-disubstituted α-amino aldehydes,[8,10] both dialkylzincs and alkylmagnesium halides lead to the same *syn*-diastereomer as major product, and these results are coincident with those obtained by addition of lithium derivatives.[11]

Table 1. Addition of R_2Zn and RMgX to aziridino aldehydes **1a-b**.[a]

Entry	Aldehyde	Organometallic	Solvent	Time (h)	Yield(%)[b]	Product (*syn*/*anti*)[c]
1	**1a**	Et_2Zn	Tol/Hex.	4	55	**2a** (91/9)
2[d]	**1a**	Et_2Zn	Tol/Hex.	5	50	**2a** (90/10)
3	**1a**	EtMgBr	Et_2O	1	48	**2a** (75/25)
4	**1a**	EtMgBr	THF	2	46	**2a** (65/35)
5	**1a**	EtMgBr	THF/TMEDA	4	40	**2a** (58/42)
6	**1a**	Me_2Zn	Tol/Hex.	4	53	**3a** (76/24)
7	**1a**	MeMgI	Et_2O	3	44	**3a** (77/23)
8	**1b**	Et_2Zn	Tol/Hex.	1	71	**2b** (100)[e]
9	**1b**	EtMgBr	Et_2O	4	56	**2b** (72/28)
10	**1b**	Me_2Zn	Tol/Hex.	3	60	**3b** (100)[e]
11	**1b**	MeMgI	Et_2O	2	63	**3b**(84/16)

[a] Unless otherwise noted, reactions were run at 0°C. [b] Numbers correspond to combined yield of pure and isolated diastereoisomers. [c] The diastereomeric ratio was determined by integration of the ^{1}H-NMR spectra of the reaction mixture.[d] Reaction was run at -78°C to 0°C. [e] Only the *syn*-diastereomer was detected by ^{1}H-NMR.

This stereochemical behaviour can be interpreted from the chelation-controlled addition of organometallic compounds to the aziridino aldehydes (Figure 1).

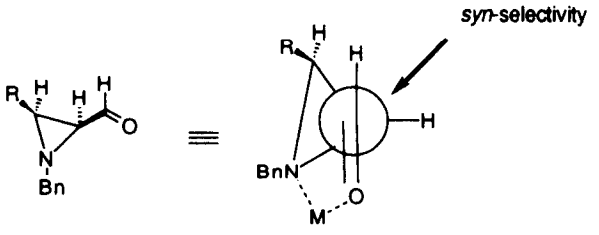


Figure 1

The threonine-derived formyl aziridine **1b** with a methyl group at C-3 *cis* to the formyl substituent in the heterocycle, reacts with diethyl- or dimethylzinc leading stereospecifically to **2b** or **3b** (entries 8 and 10), and with ethylmagnesium bromide and methylmagnesium iodide giving the *syn*-diastereomers **2b** and **3b** as major diastereomers. These results further support the proposal that the addition occurs at the least hindered *si*-face of the aldehyde in the chelated complex. Otherwise, the better stereodiferentiation observed for the less reactive zinc derivatives can also interpreted from the proposed model because the coordination to the nitrogen atom is necessary for dialkylzincs to react with aldehydes.[12]

The diastereoisomeric aziridino alcohols were separated by flash chromatography (silica gel, hexane/EtOAc: 6/1) and the stereochemistry was determined by ^{1}H-NMR spectroscopy. The resonances for the methine proton at the hydroxyl-bearing carbon in the *syn*-diastereomers appear upfield relative to the same proton in *anti*-diastereomers, whereas the vicinal coupling constant between this methine proton and that attached to the carbon of the aziridine nucleous for *syn*-**2a-2b**, and *syn*-**3a** were larger than for *anti*-**2a-b**, and *anti*-**3a** but smaller for *syn*-**3b** than for *anti*-**3b**.[2b,13] (Table 2).

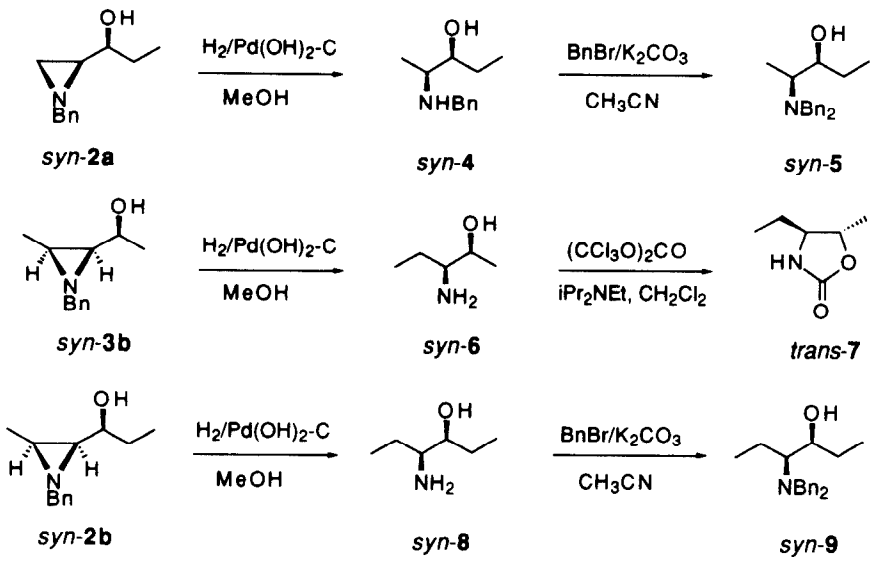
Table 2. Selected ^{1}H-NMR data for aziridino alcohols *syn*- and *anti*.

Entry	Compound	R	$J^{1,2}$(NCH-CHOH) (Hz)	δ_{CHOH}
1	*syn*-**2a**	H	4.9	3.18
2	*anti*-**2a**	H	2.9	3.65
3	*syn*-**3a**	H	4.7	3.41
4	*anti*-**3a**	H	3.5	3.87
5	*syn*-**2b**	Me	6.3	3.29
6	*anti*-**2b**	Me	4.8	3.47
7	*syn*-**3b**	Me	6.9	3.52
8	*anti*-**3b**	Me	7.1	3.70

To confirm the proposed absolute stereochemistry, the major *syn*-diastereomers **2a**, **2b** and **3b** were transformed into the known aminoalcohols *syn*-**5**, *syn*-**6** and *syn*-**9**. To this end, *syn*-**2a** was subjected to reductive ring opening[14] by stirring at r.t. with hydrogen and 20% $Pd(OH)_2$ on carbon to give *syn*-**4** as a single product in 70% yield after isolation and purification. Treatment of *syn*-**4** with benzyl bromide and K_2CO_3 in acetonitrile afforded *syn*-**5**[8] quantitatively.

It is noteworthy than *anti*-**2a** behaved in a different way to *syn*-**2a**; under similar reactions conditions *anti*-**2a** lead to 1:3 mixture (61% combined yield) of debenzylated *anti*-**2a** and (2S, 3R)-2-amino-3-pentanol.[8] In this case debenzylation occurred easier than the hydrogenolytic ring opening.

In the same way, *syn*-**3b** was transformed into a 3:7 mixture of debenzylated *syn*-**3b** and the aminoalcohol *syn*-**6** (81% combined yield), which was converted into the *trans*-oxazolidinone *trans*-**7**[8] by reaction with triphosgene/iPr_2NEt in dichloromethane,[15] and *syn*-**2b** was hydrogenolyzed to a 2:1 mixture of debenzylated *syn*-**2b** and the aminoalcohol *syn*-**8** (92% combined yield), which was dibenzylated to *syn*-**9** by treatment with excess benzyl bromide in acetonitrile.



Scheme 2

In addition, the absolute stereochemistry of (2S, 3S)-3-amino-2-pentanol (*syn*-**6**) and (3S, 4S)-4-N,N-dibenzylamino-3-hexanol (*syn*-**9**) was confirmed by diastereoselective addition of dimethylzinc and diethylzinc to (S)-2-N,N-dibenzylaminobutanal respectively.[8]

Experimental Section

General. The reactions were carried out in oven-dried glassware, under argon atmosphere, and using anhydrous solvents. Diethylzinc, as 1M solution in hexane and dimethylzinc as 2M solution in toluene, were purchased from Aldrich. The ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were registered on a Bruker AC 300 or Bruker AMX 300, using TMS as internal standard. IR spectra were recorded on a Philips PU 9706 Spectrometer, as film or KBr dispersion. Optical rotations were measured on a Perkin-Elmer 241 Polarimeter in a 1 dm. cell.

Oxidation of N-benzylaziridinoalcohols to N-benzylaziridinoaldehydes **1**.[9] To a stirred solution of oxalyl chloride (7.45 mmol, 0.65 mL) in dichloromethane (15 mL) at -78 °C under argon was added dimethyl sulfoxide (15.5 mmol, 1.1 mL). After 15 min, a solution of the corresponding N-benzylaziridinoalcohol (6.0 mmol) in dichloromethane (15 mL) was added. The mixture was stirred for 30 min and triethylamine (15.8 mmol, 2.2 mL) was added and the resulting mixture was then partitioned between dichloromethane and saturated

aqueous $NaHCO_3$. The organic phase was dried ($MgSO_4$) and concentrated to yield an oil that was used without further purification in the next step.

(2S)-1-Benzyl-2-aziridinecarboxaldehyde (1a). Colorless oil. $[\alpha]^{23}_D$= -41.6 (c= 0.9, $CHCl_3$). IR (film): 1720, 730, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.92 (d, 1H, J= 6.6 Hz, C<u>H</u>HN); 2.21 (ddd, 1H, J_1= 6.6 Hz, J_2= 6.3 Hz, J_3= 2.6 Hz, C<u>H</u>CHO); 2.28 (d, 1H, J= 2.6 Hz, CH<u>H</u>N); 3.49 (d, 1H, J= 13.3 Hz, C<u>H</u>HPh); 3.58 (d, 1H, J= 13.3 Hz, CH<u>H</u>Ph); 7.25-7.40 (m, 5H, <u>H</u>ar); 8.92 (d, 1H, J= 6.3 Hz, C<u>H</u>O). ^{13}C-NMR ($CDCl_3$): 32.6 (<u>C</u>H_2N); 44.5 (<u>C</u>HN); 63.3 (<u>C</u>H_2Ph); 127.5, 127.9, 128.5 (<u>C</u>Har); 137.5 (<u>C</u>ar); 199.7 (<u>C</u>HO). Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.18; H, 6.66 ; N, 8.47.

(2S, 3S)-1-Benzyl-3-methyl-2-aziridinecarboxaldehyde (1b). Colorless oil. $[\alpha]^{23}_D$= -141.2 (c= 1.1, $CHCl_3$). IR (film): 1700, 730, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.37 (d, 3H, J= 5.6 Hz, C<u>H</u>$_3$); 2.16 (m, 2H, C<u>H</u>CH_3, C<u>H</u>CHO); 3.58 (d, 1H, J= 13.6 Hz, CH<u>H</u>Ph); 3.62 (d, 1H, J= 13.6 Hz, C<u>H</u>HPh); 7.25-7.40 (m, 5H, <u>H</u>ar); 9.35 (d, 1H, J= 6.1 Hz, C<u>H</u>O). ^{13}C-NMR ($CDCl_3$): 14.3 (<u>C</u>H_3); 43.1 (<u>C</u>HCH_3); 48.7 (<u>C</u>HCHO); 63.0 (<u>C</u>H_2Ph); 127.0, 127.5, 128.1 (<u>C</u>Har); 137.7 (<u>C</u>ar); 200.7 (<u>C</u>HO). Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.09; H, 7.40 ; N, 7.76.

Alkylation of N-Benzylaziridinoaldehydes **1** *with R_2Zn. General method.* A 50 mL oven-dried flask equipped with a septum, a magnetic stirrer and purged with argon, was charged with the corresponding N-Benzylaziridinoaldehyde (2 mmol) and anhydrous toluene (10 mL). The solution was cooled to 0 °C (ice bath), and a 1M solution of diethyl zinc in hexane (4 mmol, 4 mL, 2 equiv.) or a 2M solution of dimethyl zinc in toluene (4 mmol, 2 mL, 2 equiv.) were injected through the septum. The mixture was stirred at that temperature until the reaction was finished (TLC), and then quenched with aqueous saturated solution of ammonium chloride (40 mL). The organic layer was separated and the aqueous phase was extracted with diethyl ether (3x 20 mL). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. The solvents were removed on Rotavapor and the residue was purified by flash chromatography (silica gel, hexane/ethyl acetate: 6/1).

Alkylation of N-Benzylaziridinoaldehydes **1** *with RMgX. General method.* To a solution of RMgBr (2.4 mmol, 1.2 equiv.) in ether (5 mL) at 0°C was added dropwise a solution of aminoaldehyde **1** (2 mmol) in ether (3 mL). The mixture was stirred for 1h and saturated NH_4Cl (10 mL) was added. The mixture was extracted with ether (3 x 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated under vacuum. The residue was purified by flash chromatography (silica gel, hexane/ethyl acetate: 6/1).

(1S, 2'S)-1-(1'-Benzyl-2'-aziridinyl)-1-propanol (*syn*-2a). Colorless oil. $[\alpha]^{23}_D$= +62.5 (c= 1.1, $CHCl_3$). IR (film): 3400, 730, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.92 (t, 3H, J= 7.4 Hz, C<u>H</u>$_3$); 1.47 (dq, 2H, J_1= 7.4 Hz, J_2= 6.3 Hz, C<u>H</u>$_2$$CH_3$); 1.51 (d, 1H, J= 6.5 Hz, C<u>H</u>HN); 1.65 (ddd, 1H, J_1= 6.5 Hz, J_2= 4.9 Hz, J_3= 3.6 Hz, C<u>H</u>N); 1.84 (d, 1H, J= 3.6 Hz, CH<u>H</u>N); 2.35 (br s, 1H, O<u>H</u>); 3.18 (dt, J_1= 6.3 Hz, J_2= 4.9 Hz, C<u>H</u>OH); 3.40 (d, 1H, J= 13.0 Hz, C<u>H</u>HPh); 3.50 (d, 1H, J=13.0 Hz, CH<u>H</u>Ph); 7.25-7.35 (m, 5H, <u>H</u>ar). ^{13}C-NMR ($CDCl_3$): 9.8 (<u>C</u>H_3); 28.2 (<u>C</u>$H_2$$CH_3$); 31.8 (<u>C</u>$H_2$N); 43.6 (<u>C</u>HN); 64.0 (<u>C</u>H_2Ph); 72.9 (<u>C</u>HOH); 127.1, 128.1, 128.3 (<u>C</u>Har); 138.7 (<u>C</u>ar). Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 74.96; H, 8.78 ; N, 7.21.

(1R, 2'S)-1-(1'-Benzyl-2'-aziridinyl)-1-propanol (*anti*-2a). Colorless oil. $[\alpha]^{23}_D$= -13.2 (c= 1.1, $CHCl_3$). IR (film): 3400, 740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.95 (t, 3H, J= 7.4 Hz, C<u>H</u>$_3$); 1.39 (d, 1H, J= 6.4 Hz, C<u>H</u>HN); 1.46 (m, 2H, C<u>H</u>$_2$$CH_3$); 1.70 (ddd, 1H, J_1= 6.4 Hz, J_2= 3.6 Hz, J_3= 2.9 Hz, C<u>H</u>N); 1.92 (d,

1H, J= 3.6 Hz, CHHN); 2.60 (br s, 1H, OH); 3.43 (d, 1H, J= 13.4 Hz, CHHPh); 3.58 (d, 1H, J= 13.4 Hz, CHHPh); 3.65 (m, 1H, CHOH); 7.25-7.40 (m, 5H, Har). ^{13}C-NMR ($CDCl_3$): 9.6 (CH_3); 27.5 (CH_2CH_3); 29.5 (CH_2N); 42.4 (CHN); 63.6 (CH_2Ph); 69.5 (CHOH); 127.1, 127.8, 128.3 (CHar); 138.8 (Car). Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.08 ; H, 9.03 ; N, 7.04 .

(1S, 2'S)-1-(1'-Benzyl-2'-aziridinyl)-1-ethanol (*syn*-3a). Colorless solid, m.p. 102-104 °C (from hexane). $[\alpha]^{23}_D$= +5.7 (c= 1.1, $CHCl_3$). IR (film): 3380, 740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.14 (d, 3H, J= 6.5 Hz, CH_3); 1.48 (d, 1H, J= 6.5 Hz, CHHN); 1.63 (ddd, 1H, J_1= 6.5 Hz, J_2= 4.7 Hz, J_3= 3.5 Hz, CHN); 1.81 (d, 1H, J= 3.5 Hz, CHHN); 2.72 (br s, 1H, OH); 3.40 (d, 1H, J= 13.0 Hz, CHHPh); 3.41 (dq, 1H, J_1= 6.5 Hz, J_2= 4.7 Hz, CHOH); 3.48 (d, 1H, J= 13.0 Hz, CHHPh); 7.25-7.35 (m, 5H, Har). ^{13}C-NMR ($CDCl_3$): 20.5 (CH_3); 31.5 (CH_2N); 45.4 (CHN); 64.0 (CH_2Ph); 68.0 (CHOH); 127.1, 128.1, 128.3 (CHar); 138.6 (Car). Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.24 ; H, 8.60 ; N, 7.60 .

(1R, 2'S)-1-(1'-Benzyl-2'-aziridinyl)-1-ethanol (*anti*-3a). Colorless oil. $[\alpha]^{23}_D$= -19.8 (c= 0.5, $CHCl_3$). IR (film): 3360, 740, 695 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.13 (d, 3H, J= 6.2 Hz, CH_3); 1.40 (d, 1H, J= 6.4 Hz, CHHN); 1.68 (ddd, 1H, J_1= 6.4 Hz, J_2= 3.6 Hz, J_3= 3.5 Hz, CHN); 1.91 (d, 1H, J= 3.6 Hz, CHHN); 2.77 (br s, 1H, OH); 3.42 (d, 1H, J= 13.3 Hz, CHHPh); 3.61 (d, 1H, J= 13.3 Hz, CHHPh); 3.87 (dq, 1H, J_1= 6.2 Hz, J_2= 3.5 Hz, CHOH); 7.25-7.40 (m, 5H, Har). ^{13}C-NMR ($CDCl_3$): 19.9 (CH_3); 29.45 (CH_2N); 43.6 (CHN); 63.6 (CH_2Ph); 64.5 (CHOH); 127.1, 127.9, 128.3 (CHar); 138.8 (Car). Calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.32 ; H, 8.38 ; N, 7.68 .

(1S, 2'S, 3'S)-1-(1'-Benzyl-3'-methyl-2'-aziridinyl)-1-propanol (*syn*-2b). Colorless oil. $[\alpha]^{23}_D$= +23.0 (c=0.9, $CHCl_3$). IR (film): 3300, 730, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.94 (t, 3H, J= 7.5 Hz, CH_3CH_2); 1.20 (d, 3H, J= 5.9 Hz, CH_3CH); 1.52 (m, 2H, CH_2CH_3); 1.55 (dd, 1H, J_1= 6.8 Hz, J_2= 6.3 Hz, CHCHOH); 1.77 (dq, 1H, J_1= 6.8 Hz, J_2= 5.9 Hz, $CHCH_3$); 2.49 (br s, 1H, OH); 3.29 (dt, 1H, J_1= 6.8 Hz, J_2= 6.3 Hz,CHOH); 3.47 (d, 1H, J= 13.2 Hz, CHHPh); 3.54 (d, 1H, J= 13.2 Hz, CHHPh) ; 7.25-7.40 (m, 5H, Har). ^{13}C-NMR ($CDCl_3$): 9.6 (CH_3CH_2); 13.6 (CH_3CH); 28.3 (CH_2CH_3); 39.6 ($CHCH_3$); 48.7 (CHCHOH); 64.2 (CH_2Ph); 69.7 (CHOH); 126.9, 127.9, 128.3 (CHar); 138.9 (Car). Calcd. for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.82 ; H, 9.18 ; N, 6.59 .

(1R, 2'S, 3'S)-1-(1'-Benzyl-3'-methyl-2'-aziridinyl)-1-propanol (*anti*-2b). Colorless oil. $[\alpha]^{23}_D$= -4.7 (c= 0.8, $CHCl_3$). IR (film): 3380, 740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.93 (t, 3H, J= 7.4 Hz, CH_3CH_2); 1.28 (d, 3H, J= 5.8 Hz, CH_3CH); 1.47 (m, 2H, CH_2CH_3); 1.56 (m, 1H, CHCHOH); 1.71 (dq, 1H, J_1= 6.4 Hz, J_2= 5.8 Hz, $CHCH_3$); 2.27 (br s, 1H, OH); 3.47 (dt, 1H, J_1= 7.4 Hz, J_2= 4.8 Hz, CHOH); 3.51 (s, 2H, CH_2Ph); 7.25-7.40 (m, 5H, Har). ^{13}C-NMR ($CDCl_3$): 9.7 (CH_3CH_2); 13.7 (CH_3CH); 28.3 (CH_2CH_3); 39.2 ($CHCH_3$); 46.9 (CHCHOH); 64.3 (CH_2Ph); 70.7 (CHOH); 127.0, 128.0, 128.3 (CHar); 138.9 (Car). Calcd. for $C_{13}H_{19}NO$: C, 76.06; H, 9.33; N, 6.82. Found: C, 75.73 ; H, 9.22 ; N, 6.76 .

(1S, 2'S, 3'S)-1-(1'-Benzyl-3'-methyl-2'-aziridinyl)-1-ethanol (*syn*-3b). Colorless oil. $[\alpha]^{23}_D$= +13.5 (c= 1, $CHCl_3$). IR (film): 3300, 730, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.18 (d, 3H, J= 6.4 Hz, CH_3CHOH); 1.20 (d, 3H, J= 5.8 Hz, CH_3CHN); 1.55 (dd, 1H, J= 6.9 Hz, J= 6.8 Hz, CHCHOH); 1.74 (dq, 1H, J= 6.8 Hz, J= 5.8 Hz, CH_3CHN); 2.80 (br s, 1H, OH); 3.46 (d, 1H, J= 13.3 Hz, CHHPh); 3.52 (dq, 1H, J= 6.9 Hz, J= 6.4 Hz, CHOH); 3.54 (d, 1H, J= 13.3 Hz, CHHPh); 7.25-7.40 (m, 5H, Har). ^{13}C-NMR ($CDCl_3$): 13.5 (CH_3CHN); 20.9 (CH_3CHOH); 39.6 ($CHNCH_3$); 49.8 (CHCHOH); 64.4 (CH_2Ph); 65.5 (CHOH); 127.1, 128.0, 128.5 (CHar); 139.1 (Car). Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.03; H, 9.00 ; N, 7.04 .

(1R, 2'S, 3'S)-1-(1'-Benzyl-3'-methyl-2'-aziridinyl)-1-ethanol (*anti*-3b). Colorless oil. $[\alpha]^{23}_D$= +4.2 (c= 0.24, $CHCl_3$). IR (film): 3350, 730, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.14 (d, 3H, J= 6.2 Hz, $C\underline{H}_3CHOH$); 1.29 (d, 3H, J= 5.8 Hz, $C\underline{H}_3CHN$), 1.52 (dd, 1H, J=7.1 Hz, J= 6.4 Hz, C<u>H</u>CHOH); 1.72 (dq, 1H, J=6.4 Hz, J=5.8 Hz, $CH_3C\underline{H}N$); 2.31 (br s, 1H, O<u>H</u>); 3.42 (d, 1H, J= 13.2 Hz, C<u>H</u>HPh); 3.60 (d, 1H, J= 13.2 Hz, CH<u>H</u>Ph); 3.70 (dq, 1H, J= 7.1 Hz, J= 6.2 Hz, C<u>H</u>OH); 7.20-7.40 (m, 5H, <u>H</u>ar). ^{13}C-NMR ($CDCl_3$): 13.6 ($\underline{C}H_3CHN$); 21.1 ($\underline{C}H_3CHOH$); 39.6 ($CH_3\underline{C}HN$); 48.2 (<u>C</u>HCHOH); 64.3 ($\underline{C}H_2Ph$); 65.6 (<u>C</u>HOH); 127.0, 128.1, 128.3 (<u>C</u>Har); 138.9 (<u>C</u>ar). Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.11 ; H, 8.74 ; N, 7.20 .

(2S, 3S)-2-Benzylamino-3-pentanol (*syn*-4). Colorless oil. $[\alpha]^{23}_D$= +36.8 (c= 0.7, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): 1.00 (t, 3H, J= 7.4 Hz, $C\underline{H}_3CH_2$); 1.12 (d, 3H, J= 6.4 Hz, $C\underline{H}_3CH$); 1.38 (m, 1H, C<u>H</u>HCH$_3$); 1.64 (m, 1H, CH<u>H</u>CH$_3$); 2.52 (dq, 1H, J_1= 8.1 Hz, J_2= 6.4 Hz, C<u>H</u>N); 2.75 (br s, 1H, O<u>H</u>); 3.16 (dt, 1H, J_1= 8.1 Hz, J_2= 3.2 Hz, C<u>H</u>OH); 3.71 (d, 1H, J= 12.9 Hz, C<u>H</u>HPh); 3.94 (d, 1H, J= 12.9 Hz, CH<u>H</u>Ph); 7.25-7.35 (m, 5H, <u>H</u>ar). ^{13}C-NMR ($CDCl_3$): 9.9 ($\underline{C}H_3CH_2$); 16.4 ($\underline{C}H_3CH$); 26.4 ($\underline{C}H_2CH_3$); 51.1 ($\underline{C}H_2Ph$); 57.2 (<u>C</u>HN); 75.7 (<u>C</u>HOH); 127.1, 128.1, 128.4 (<u>C</u>Har); 139.9 (<u>C</u>ar).

(2S, 3S)-3-Amino-2-pentanol (*syn*-6). Colorless solid, m.p. 48-50 °C (from hexane). $[\alpha]^{23}_D$= -5.4 (c= 0.9, MeOH). IR (film): 3340, 1455, 1375, 1110, 960 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.96 (t, 3H, J= 7.4 Hz, $C\underline{H}_3CH_2$); 1.17 (d, 3H, J= 6.2 Hz, $C\underline{H}_3CH$); 1.24 (m, 1H, C<u>H</u>HCH$_3$); 1.60 (m, 1H, CH<u>H</u>CH$_3$); 2.40 (m, 1H, C<u>H</u>N); 2.52 (br s, 3H, O<u>H</u> and N<u>H</u>$_2$); 3.45 (dt, 1H, J_1= 6.7 Hz, J_2= 6.2 Hz C<u>H</u>OH). ^{13}C-NMR ($CDCl_3$): 10.4 ($\underline{C}H_3CH_2$); 20.0 ($\underline{C}H_3CH$); 26.7 ($\underline{C}H_2$); 58.9 (<u>C</u>HN); 69.8 (<u>C</u>HOH).

(4S, 5S)-4-Ethyl-5-methyloxazolidin-2-one (*trans*-7). Colorless oil. $[\alpha]^{23}_D$= -39.7 (c= 0.9, $CHCl_3$). IR (film): 3260, 1735 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.96 (t, 3H, J= 7.4 Hz, $C\underline{H}_3CH_2$); 1.42 (d, 3H, J= 6.3 Hz, $C\underline{H}_3CH$); 1.59 (m, 2H, $C\underline{H}_2$); 3.34 (m, 1H, C<u>H</u>N); 4.30 (dq, 1H, J= 6.3 Hz, J= 5.9 Hz, C<u>H</u>O); 6.88 (br s, 1H, N<u>H</u>). ^{13}C-NMR ($CDCl_3$): 9.5 ($\underline{C}H_3CH_2$); 20.3 ($\underline{C}H_3CH$); 27.7 ($\underline{C}H_2$); 61.0 (<u>C</u>HN); 78.6 (<u>C</u>HO); 159.7 (<u>C</u>O).

(3S, 4S)-4-N,N-Dibenzylamino-3-hexanol (*syn*-9). Colorless oil. $[\alpha]^{23}_D$= +17.5 (c= 1.2, $CHCl_3$). IR (film): 3380, 1600, 1450, 740, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.91 (t, 3H, J= 7.2 Hz, $C\underline{H}_3$); 1.08 (t, 3H, J= 7.2 Hz, $C\underline{H}_3$); 1.15 (m, 1H, C<u>H</u>HCH$_3$); 1.35 (m, 1H, C<u>H</u>HCH$_3$); 1.57 (m, 1H, CH<u>H</u>CH$_3$); 1.77 (m, 1H, CH<u>H</u>CH$_3$); 2.37 (m, 1H, C<u>H</u>N); 3.40 (m, 1H, C<u>H</u>OH); 3.45 (d, 2H, J= 13.2 Hz, C<u>H</u>HPh); 3.87 (d, 2H, J= 13.2 Hz, CH<u>H</u>Ph); 4.40 (br s, 1H, O<u>H</u>); 7.20-7.35 (m, 10H, <u>H</u>arom). ^{13}C-NMR ($CDCl_3$): 10.1 ($\underline{C}H_3$); 14.0 ($\underline{C}H_3$); 19.0 ($\underline{C}H_2$); 26.8 ($\underline{C}H_2$); 54.0 ($\underline{C}H_2Ph$); 64.1 (<u>C</u>HN); 71.6 (<u>C</u>HOH); 127.1, 128.4, 129.1 (<u>C</u>Harom); 139.0 (<u>C</u>arom).

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