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Chemoenzymatic Synthesis of Chiral β-Azidoalcohols. Application to the Preparation of Chiral Aziridines and Aminoalcohols

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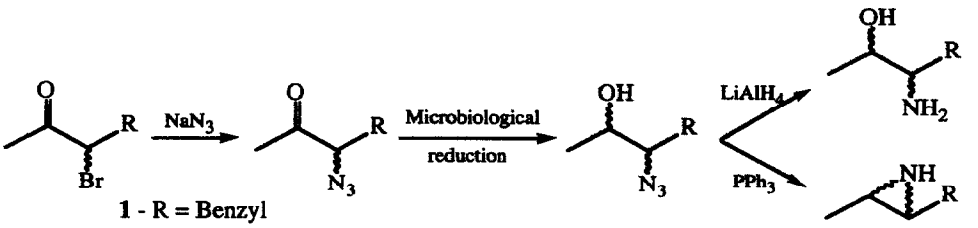
Abstract : From the microbiological reduction of 3-azido-2-octanone, 3-azido-4-phenyl-2-butanone and 1-azido-1-phenyl-2-propanone, homochiral isomers of the corresponding β-azidoalcohols were prepared. These "α-bichiral" synthons were used to prepare all the stereoisomers of 2-methyl-3-*n*-pentylaziridine and 2-methyl-3-benzylaziridine and some homochiral aminoalcohols.

Within our research concerning the study of new bioconversion reactions, we have been interested in the microbiological reduction of α-substituted ketones in order to obtain alcohols having two vicinal stereogenic carbon atoms. These alcohols are known as "α-bichiral" synthons. Having studied the microbiological reduction of α-halogenated ketones, which allowed us to synthesize homochiral 2,3-epoxides in three steps[1,2], we wanted to change the nature of the substituent. Vicinal azidoalcohols are the direct precursors of aminoalcohols, whose structure is present in numerous natural products[3], and aziridines. Up to now, the described syntheses of homochiral azidoalcohols have used either the opening of homochiral epoxides[4] or the conversion of homochiral β-diols[5]. The method of Matteson *et al.*[6], using homochiral boronic esters, is the only one which yields homochiral azidoalcohols directly, but it contains a large number of steps resulting in a low overall yield. We thought that the microbiological reduction of α-azidoketones would allow the preparation of the corresponding azidoalcohols, with a good yield and in fewer steps.

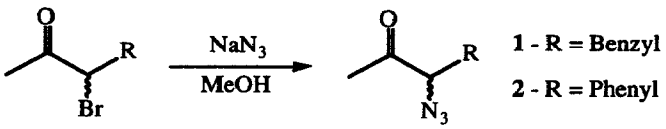
In previous work, the microbiological reduction of 3-azido-2-octanone was studied, and we showed that all the homochiral isomers of 3-azido-2-octanol could be prepared[1]. In this paper, the results of the microbiological reduction of two other azidoketones : 3-azido-4-phenyl-2-butanone (R = benzyl) and 1-azido-1-phenyl-2-propanone (R = phenyl), will be developed as well as the preparation of the homochiral isomers of some aziridines and aminoalcohols. The general scheme of the synthesis is the following one :



1 - R = Benzyl
2 - R = Phenyl

I - Microbiological reduction of α-azidoketones

3-Azido-4-phenyl-2-butanone **1** and 1-azido-1-phenyl-2-propanone **2** were prepared from the corresponding bromoketones previously described[2] according to Effenberger *et al.*[7]. A methanolic solution of bromoketone was treated with sodium azide. The yields were 95 % for **1** and 90 % for **2**.



The study of the microbiological reduction of these two azidoketones was realized with the same microorganisms as those previously used for the reduction of α-halogenoketones[1,2] : the yeasts (*Saccharomyces cerevisiae* and *Rhodotorula glutinis*), the fungi (*Aspergillus niger*, *Beauveria sulfurescens*, *Cunninghamella elegans*, *Geotrichum candidum*, *Mortierella isabellina* and *Sporotrichum exile*) and the bacterium (*Lactobacillus kefir*). The bakers' yeast (*S. cerevisiae*) was used freeze-dried under non-fermenting conditions, *i.e.* suspended in water without adding sugar. The bioconversions with the other microorganisms were done with washed resting cells, except for *R. glutinis*. Growing cells were used for this microorganism.

For each azidoketone, a kinetic study was conducted with each microorganism. These studies allowed us to determine the best conditions for the bioconversion (choice of the microorganism, incubation time).

1 - Microbiological reduction of 3-azido-4-phenyl-2-butanone

The kinetic studies showed that all the microorganisms reduced 3-azido-4-phenyl-2-butanone and yielded a mixture of two diastereoisomeric azidoalcohols. Quantitative assays were carried out for 24 or 48 hours incubation time with each microorganism. The resultant azidoalcohols were purified, and their absolute configurations and enantiomeric excesses were determined. The results are collected in Table I.

The incubation period was 24 hours except for *B. sulfurescens* and *C. elegans* where it was 48 hours. The proportions of each diastereoisomer and the overall yield after work-up are recorded in the last column of the table. The diastereoisomeric azidoalcohols were separated and purified by chromatography on a silica column.

Generally, equivalent amounts of *syn* and *anti* diastereoisomers were obtained except in the case of *B. sulfurescens* and *S. exile* for which the *anti* diastereoisomer constituted the main product. Unfortunately, the enantiomeric excesses were low (16 %) or not excellent (89 %). The best enantiomeric excesses (≥ 98 %) were obtained for the (2S,3S) and (2S,3R) isomers with bakers' yeast, *M. isabellina* and *R. glutinis* and for

(2R,3R) with *L. kefir* and *A. niger*. The (2R,3S) diastereoisomer was more difficult to obtain enantiomerically pure : the best enantiomeric excess obtained with *A. niger* was 82 %.

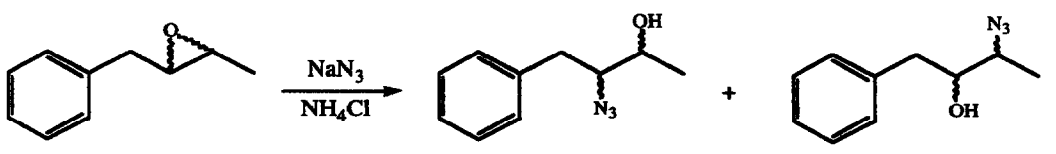
Table I : Microbiological reduction of 3-azido-4-phenyl-2-butanone

	syn Azidoalcohol			*anti* Azidoalcohol			Yield
	$[\alpha]_J^{25}$	e.e.	Conf.	$[\alpha]_J^{25}$	e.e.	Conf.	
Bakers' yeast	+ 4	≥ 98 %	(2S,3S)	+ 16	≥ 98 %	(2S,3R)	72 % (55/45)
Mortierella isabellina	+ 4	≥ 98 %	(2S,3S)	+ 15	98 %	(2S,3R)	75 % (55/45)
Rhodotorula glutinis	+ 4	≥ 98 %	(2S,3S)	+ 16	≥ 98 %	(2S,3R)	95 % (45/55)
Beauveria sulfurescens	+ 1	26 %	(2S,3S)	- 2	16 %	(2R,3S)	60 % (30/70)
Sporotrichum exile	+ 2	52 %	(2S,3S)	+ 14	89 %	(2S,3R)	60 % (30/70)
Lactobacillus kefir	- 4	≥ 98 %	(2R,3R)	- 11	72 %	(2R,3S)	75 % (45/55)
Aspergillus niger	- 4	≥ 98 %	(2R,3R)	- 13	82 %	(2R,3S)	75% (50/50)
Cunninghamella elegans	- 3	81 %	(2R,3R)	- 11	72 %	(2R,3S)	50 % (45/55)
Geotrichum candidum	- 4	≥ 98 %	(2R,3R)	- 7	45 %	(2R,3S)	50 % (50/50)

In each case, the yield of bioconversion was high. Thus by carefully choosing the microorganism, one can obtain all the isomers of 3-azido-4-phenyl-2-butanol in good yields and excellent enantiomeric excesses.

The enantiomeric excesses were determined by gas phase chromatography of the esters obtained from the reaction of each azidoalcohol with (-)-(S)-O-acetyllactyl chloride. The proportion of each diastereoisomeric ester was measured, and the enantiomeric excesses were calculated for each azidoalcohol.

No isomer of 3-azido-4-phenyl-2-butanol has been described in the literature. To determine the absolute configuration of the azidoalcohols formed during the microbiological reduction, two isomeric azidoalcohols synthesized from homochiral epoxides, were compared to the microbiologically-derived ones.



Indeed, the syntheses and the absolute configurations of all the isomers of 4-phenyl-2,3-epoxybutane have been previously reported[2]. By the ring-opening of these epoxides with sodium azide, two isomers of 3-azido-4-phenyl-2-butanol were prepared. The absolute configuration of the starting epoxide and the stereochemistry of the reaction being known, the configuration of the resultant azidoalcohol could be assigned easily.

The ring-opening of the epoxide is not regioselective, and it yields a mixture of 2-azido-4-phenyl-3-butanol and 3-azido-4-phenyl-2-butanol. The reaction takes place with inversion of configuration at the azide-bearing carbon atom. So from the (2S,3S)-4-phenyl-2,3-epoxybutane, a mixture of 80 % (2R,3S)-2-azido-4-phenyl-3-butanol and 20 % (2S,3R)-3-azido-4-phenyl-2-butanol was obtained, and from (2S,3R)-4-phenyl-2,3-epoxybutane, 63 % (2R,3R)-2-azido-4-phenyl-3-butanol and 37 % (2S,3S)-3-azido-4-phenyl-2-butanol were formed. The specific rotations of these azidoalcohols are reported in Table II.

Table II : Synthesis of 4-phenylazidobutanols from opening of epoxides

4-Phenyl-2,3-epoxybutane	2-Azido-4-phenyl-3-butanol			3-Azido-4-phenyl-2-butanol			
Configuration	Configuration	$[\alpha]_J^{25}$	ee	Configuration	$[\alpha]_J^{25}$	ee	Yield
(2S,3R)	(2R,3R)	- 45	≥ 98 %	(2S,3S)	+ 4	≥ 98 %	96 % (63/37)
(2S,3S)	(2R,3S)	- 61	≥ 98 %	(2S,3R)	+ 16	≥ 98 %	92 % (80/20)

By comparing the sign of the specific rotation of 3-azido-4-phenyl-2-butanol coming from the microbiological reduction with that coming from the epoxide opening, the absolute configuration of all the isomers obtained by the microbiological reduction could be assigned.

Moreover, the ring-opening of epoxides constitutes another excellent chemoenzymatic method to prepare the isomers of 2-azido-4-phenyl-3-butanol in good yields and excellent enantiomeric excesses.

2 - Microbiological reduction of 1-azido-1-phenyl-2-propanone

The results of the analytical assays showed that all the microorganisms reduced 1-azido-1-phenyl-2-propanone except *C. elegans* and *S. exile* which were not used for quantitative assays. The results of the quantitative assays are collected in Table III. In each case, the incubation time is 24 hours. The yields correspond to the total amount of azidoalcohols obtained after work-up. The ratio of the two diastereoisomers is indicated in brackets.

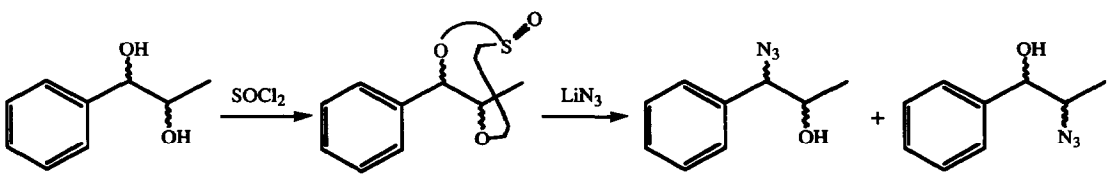
The diastereoisomeric azidoalcohols were separated by chromatography on a silica gel column in order to determine their enantiomeric purity and their absolute configuration. Yields were generally very good, except in the case of *B. sulfurescens* and *A. niger*. Bakers' yeast, *M. isabellina*, *B. sulfurescens* and *R. glutinis* yielded the (1S,2S) and (1R,2S) isomers with excellent enantiomeric excesses. However, *R. glutinis* was the microorganism which gave the best results, because both the (1S,2S) and (1S,2R) isomers were obtained in very good yields and excellent enantiomeric excesses. *A. niger*, which usually gives alcohols of (R) configuration, changed its enantiogenicity and gave here the (S) alcohol with a low enantiomeric excess. Only *L. kefir* yielded alcohols of (R) configuration with a medium enantiomeric excess (70 %) for the (1R,2R)

isomer and a very low enantiomeric excess for the *anti* (1S,2R) isomer. It would be necessary to try other microbiological strains in order to obtain these two diastereoisomers enantiomerically pure. The enantiomeric excesses were determined by direct analysis of each azidoalcohol with gas phase chromatography on a chiral column : Lipodex E (modified γ-cyclodextrins).

Table III : Microbiological reduction of 1-azido-1-phenyl-2-propanone

	syn Azidoalcohol			*anti* Azidoalcohol			Yield
	$[\alpha]_J^{25}$	e.e.	Conf.	$[\alpha]_J^{25}$	e.e.	Conf.	
Bakers' yeast	+ 250	≥ 98 %	(1S,2S)	- 206	≥ 98 %	(1R,2S)	60 % (20/80)
Mortierella isabellina	+ 250	≥ 98 %	(1S,2S)	- 206	≥ 98 %	(1R,2S)	90 % (40/60)
Beauveria sulfurescens	+ 250	≥ 98 %	(1S,2S)	- 202	98 %	(1R,2S)	40 % (15/85)
Rhodotorula glutinis	+ 250	≥ 98 %	(1S,2S)	- 206	≥ 98 %	(1R,2S)	95 % (40/60)
Aspergillus niger	+ 195	78 %	(1S,2S)	- 121	59 %	(1R,2S)	40% (50/50)
Geotrichum candidum	+ 200	80 %	(1S,2S)	- 164	80 %	(1R,2S)	90 % (40/60)
Lactobacillus kefir	- 175	70 %	(1R,2R)	+ 52	24 %	(1S,2R)	85 % (55/45)

The different isomers of 1-azido-1-phenyl-2-propanol have not been described in the literature. To assign the absolute configurations of the various azidoalcohols formed, a synthesis of 1-azido-1-phenyl-2-propanols was realized from optically pure β-diols. This method has been reported already in the case of 3-azido-2-octanols[1]. The synthesis is based on the following reaction scheme :



In previous work[8], the microbiological reduction of 1-phenyl-1,2-propanedione has been reported. The authors demonstrated that by an appropriate choice of the microorganism, all the isomers of 1-phenyl-1,2-propanediol could be obtained enantiomerically pure. With the method of Lohray and Ahuja[5], a β-diol can be converted into a β-azidoalcohol. The cyclic sulfite is obtained quantitatively by the action of thionyl chloride on 1-phenyl-1,2-propanediol, and then it is cleaved in the presence of lithium azide overnight at 120°C in dimethylformamide.

We first carried out the reaction sequence on the (-)-(1S,2S)-1-phenyl-1,2-propanediol obtained by the microbiological reduction of 1-phenyl-1,2-propanedione with *Beauveria sulfurescens*[8]. We also used as starting material (-)-(1R,2S)-1-phenyl-1,2-propanediol, which is the only isomer formed during the reduction of the α-dione by bakers' yeast, when the bioconversion is realized with a high concentration of bakers' yeast[9]. From each of these β-diols, the cyclic sulfites were synthesized and cleaved by LiN_3 according to the above method. The opening of the cyclic sulfite is not regioselective : a mixture of 1-azido-1-phenyl-2-propanol and 2-azido-1-phenyl-1-propanol is obtained. The ratio of these two products depends on the *syn* or *anti* character of the starting diol. From the (1R,2S) diol, we obtained 58 % 1-azido-1-phenyl-2-propanol and 42 % 2-azido-1-phenyl-1-propanol while from the (1S,2S) diol, the proportion of these two azidoalcohols was 90 and 10 % respectively.

The absolute configuration of the azidoalcohols, obtained from the β-diols, was deduced directly from that of the diols. The cyclic sulfites had the same configuration as that of the starting diols, and the cleavage of the cycle took place with an inversion of configuration on the azide-bearing carbon atom. The results of these two syntheses are collected in Table IV.

Table IV : Synthesis of 1-phenylazidopropanols from 1-phenyl-1,2-propanediol

1-Phenyl-1,2-propanediol	2-Azido-1-phenyl-1-propanol			1-Azido-1-phenyl-2-propanol			
Configuration	Configuration	$[\alpha]_J^{25}$	ee	Configuration	$[\alpha]_J^{25}$	ee	Yield
(1R,2S)	(1R,2R)	- 140	≥ 98 %	(1S,2S)	+ 250	≥ 98 %	78 % (42/58)
(1S,2S)	(1S,2R)	- 50	≥ 98 %	(1R,2S)	- 206	≥ 98 %	75 % (10/90)

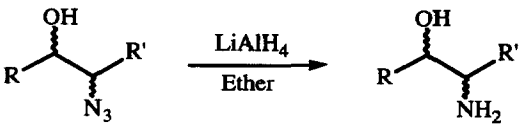
By comparing the physical constants and the specific rotations of the 1-azido-1-phenyl-2-propanols obtained from the microbiological reduction with those from the two β-diols, the absolute configuration of all the azidoalcohols from the reduction can be assigned.

The microbiological reduction of 1-azido-1-phenyl-2-propanone gave access to three isomers of the corresponding azidoalcohol. The enantiomerically pure (1S,2S) and (1R,2S) isomers were obtained with bakers' yeast, *R. glutinis* and *M. isabellina* whereas *L. kefir* yielded the (1R,2R) isomer with a 70 % enantiomeric excess.

II - Synthesis of homochiral β-aminoalcohols

The microbiological reductions of α-azidoketones described above and in our previous work[1] demonstrate that generally all the homochiral isomers of azidoalcohols can be prepared. It would be interesting to use these homochiral synthons in asymmetric synthesis. As the azide group is a direct precursor of the amino function, the azidoalcohols were converted into aminoalcohols by chemical reduction.

The reaction was carried out in ether with one equivalent of $LiAlH_4$ and led to the aminolalcohol in an excellent yield (85-95 %).



R = CH_3 R' = C_5H_{11} R = C_5H_{11} R' = CH_3

R = CH_3 R' = Benzyl R = Benzyl R' = CH_3

The diastereoisomers of 3-azido-2-octanol and of 2-azido-3-octanol, described previously[1], as well as the isomers of 3-azido-4-phenyl-2-butanol and 2-azido-4-phenyl-3-butanol, obtained respectively by microbiological reduction and from the ring-opening of 4-phenyl-2,3-epoxybutane, were converted into the corresponding aminoalcohols. The characteristics of these various aminoalcohols are collected in Table V.

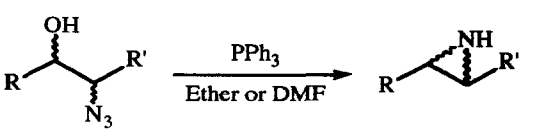
Table V : Synthesis of various aminoalcohols

	Azidoalcohols		Aminoalcohols			
	Conf.	obtained from	$[\alpha]_J^{25}$	e.e.	Conf.	Yield
R = CH_3, R' = C_5H_{11}	(2S,3S)	*B. sulfurescens*	- 11	97 %	(2S,3S)	93 %
	(2R,3R)	*L. kefir*	+ 11	97 %	(2R,3R)	90 %
	(2S,3R)	Bakers' yeast	+ 3	≥ 98 %	(2S,3R)	93 %
	(2R,3S)	*L. kefir*	- 3	≥ 98 %	(2R,3S)	90 %
R = C_5H_{11}, R' = CH_3	(2R,3R)	Cyclic sulfite	+ 14	≥ 98 %	(2R,3R)	95 %
	(2R,3S)	Cyclic sulfite	- 16	≥ 98 %	(2R,3S)	93 %
R = CH_3, R' = Benzyl	(2S,3S)	Bakers' yeast	- 27	≥ 98 %	(2S,3S)	88 %
	(2R,3R)	*A. niger*	+ 27	≥ 98 %	(2R,3R)	85 %
	(2S,3R)	*R. glutinis*	+ 35	≥ 98 %	(2S,3R)	85 %
	(2R,3S)	*A. niger*	- 29	82 %	(2R,3S)	88 %
R = Benzyl, R' = CH_3	(2R,3R)	Epoxide	+ 27	≥ 98 %	(2R,3R)	90 %
	(2R,3S)	Epoxide	- 31	≥ 98 %	(2R,3S)	90 %

The chemical reduction takes place without affecting the stereogenic centres of the azidoalcohol. Therefore, the absolute configuration of the aminoalcohol remains the same as that of the azidoalcohol from which it is derived, as it was reported by Sharpless *et al.*[5]. For the same reason, the enantiomeric excesses do not change during the reduction of the azide group. All the isomers of the aminoalcohols reported in Table V have never been described in the literature.

III - Synthesis of homochiral aziridines

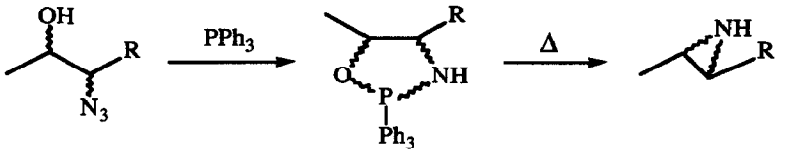
Some of the azidoalcohols were also cyclized into aziridines. The methods described in the literature use triphenylphosphine as the cyclizing reagent, the reaction solvent being either ether or DMF.



R = CH_3 R' = C_5H_{11}

R = CH_3 R' = Benzyl

Our first assays were carried out in anhydrous ether according to Ittah *et al.*[10]. The starting azidoalcohol disapeared completely but no aziridine was formed. Legters *et al.*[11] showed that the reaction scheme was the following :



The cyclic intermediate is formed very quickly, even at room temperature, but its decomposition into the aziridine requires heating at 70-80°C. Instead of using DMF, which is difficult to eliminate because of the volatility of some aziridines, the reaction was carried out at 70°C in THF. Under these conditions, the aziridine purification was very easy (particularly the elimination of triphenylphosphine oxide) : after evaporation of the THF under vacuum, the residue was purified by bulb-to-bulb distillation, and thus the pure aziridine was obtained. This reaction was carried out with the four diastereoisomers of 3-azido-2-octanol and 3-azido-4-phenyl-2-butanol coming from the microbiological reductions. The results of these syntheses are reported in Table VI. The *cis* or *trans* character of each aziridine and its absolute configuration were deduced directly from those of the starting azidoalcohols. Indeed, a *syn* azidoalcohol gave a *cis* aziridine and an *anti* azidoalcohol gave a *trans* aziridine. In these two cases, the reaction took place with inversion of configuration at the carbon atom bearing the hydroxyl group, *i.e* at the 2-carbon atom for the two azidoalcohols studied, according to Sharpless *et al.*[5]. The enantiomeric excesses were determined by analysis of the aziridines (R' = C_5H_{11}) with gas phase chromatography by direct injection on a chiral column and by ^1H NMR of the Mosher derivative for the other aziridines (R' = Benzyl).

Table VI : Synthesis of aziridines

	Azidoalcohols		Aziridines			
	Conf.	obtained from	$[\alpha]_J^{25}$	e.e.	Conf.	Yield
R = CH_3, R' = C_5H_{11}	(2S,3S)	*B. sulfurescens*	+ 1	97 %	(2R,3S)	75 %
	(2R,3R)	*L. kefir*	- 1	97 %	(2S,3R)	73 %
	(2S,3R)	Bakers' yeast	+ 57	≥ 98 %	(2R,3R)	65 %
	(2R,3S)	*L. kefir*	- 57	≥ 98 %	(2S,3S)	68 %
R = CH_3, R' = Benzyl	(2S,3S)	Bakers' yeast	- 18	≥ 98 %	(2R,3S)	70 %
	(2R,3R)	*A. niger*	+ 18	≥ 98 %	(2S,3R)	69 %
	(2S,3R)	*R. glutinis*	+ 64	≥ 98 %	(2R,3R)	75 %
	(2R,3S)	*A. niger*	- 52	82 %	(2S,3S)	70 %

The results described above show that the proposed chemoenzymatic scheme was successful for the preparation of enantiomerically pure aziridines and aminoalcohols. All the isomers of a variety of homochiral aziridines can be obtained in four steps with excellent enantiomeric excesses and good yields. The key step of this synthetic scheme was the microbiological reduction of the azidoketones which generally yielded all the enantiomerically pure isomers of the corresponding azidoalcohols by an appropriate choice of the microorganism.

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EXPERIMENTAL SECTION

1 - GENERAL METHODS

CHROMATOGRAPHY : Gas chromatography (GC) was performed using an instrument equiped with a flame ionization detector and a 50 m x 0.32 mm (or a 25 m x 0.32 mm for 2-methyl-3-benzylaziridine) capillary column coated with Carbowax 20 M for analytical analysis. A 25 m x 0.25 mm capillary column coated with modified γ-cyclodextrins (Lipodex E) was used for determining enantiomeric excesses. The carrier gas was hydrogen at 65 KPa. Oven temperatures varied according to the product and are given in each case. The progress of the reaction was sometimes followed using thin layer chromatography (TLC) with Kieselgel 60 PF plates using the same eluants as for column chromatography. Plates were developed directly using UV light or a pulverised vanilin solution or a solution of ammonium molybdate derivatives. With the latter two, the plates were passed in an oven at 140°C. Column chromatography was performed on silica gel 60 Merck (70-230 μm). Eluants varied and are indicated for each product.

SPECTROSCOPY AND ANALYTICAL METHODS : After bioconversion, the crude mixtures were analyzed by GC and the retention times of the reduction products were compared with those of chemically obtained racemates. Optical rotations of the compounds were determined at 25°C for the mercury J line (λ = 578 nm, c in g/mL). Enantiomeric excesses were determined by GC for 1-azido-1-phenyl-2-propanol and 2-methyl-3-*n*-pentylaziridine using the Lipodex E column, and for the esters of 3-azido-4-phenyl-2-butanol, obtained after reaction with (-)-(S)-O-acetyllactic chloride[12], using the Carbowax column. NMR analyses were carried out on purified compounds in $CDCl_3$, either at 300 MHz on a 300 MSL Bruker spectrometer or at 400 MHz on an AC 400 Bruker spectrometer. The chemical shifts were relative to chloroform. The Mosher derivatives were synthesized according to Foglia *et al.*[13]. High Resolution Mass Spectrometry (HRMS) and elemental analyses were performed by the Service Central d'Analyses du CNRS, Vernaison (France).

MICROBIOLOGICAL METHODS : The microorganisms were all laboratory-grown with the exception of freeze-dried bakers' yeast, which was a commercial product (ANCEL S.A. Strasbourg). Preculture and culture conditions for fungi *Aspergillus niger* ATCC 9142, *Beauveria sulfurescens* ATCC 7159, *Mortierella isabellina* NRRL 1757, *Geotrichum candidum* CBS 233-76, *Cunninghamella elegans var. elegans* ATCC 9245, *Sporotrichum exile* QM 180, for yeast *Rhodotorula glutinis* NRRL Y 1091 and bacterium *Lactobacillus kefir* DSM 20587 have been described elsewhere[2].

BIOCONVERSION CONDITIONS : Bioconversions with bakers' yeast and the other microorganisms (in metabolic resting phase except for *Rhodotorula glutinis*) were carried out as previously described[2].

2 - SUBSTRATES

3-Azido-4-phenyl-2-butanone and 1-azido-1-phenyl-2-propanone were synthesized from the corresponding bromoketones, previously described[2], following a known method[7].

To a solution of 10 mmol. of bromoketone in 3 mL of methanol, with stirring and cooling at 0°C, was added 10 mmol. (0.650 g) of sodium azide. The mixture was stirred overnight at room temperature. The methanol was then evaporated under vacuum, and the residue was diluted with water and extracted three times with ether. The organic phase was dried on $MgSO_4$. After evaporation of the solvent, we obtained the pure

azidoketone in a 95 % yield for 3-azido-4-phenyl-2-butanone and 90 % yield for 1-azido-1-phenyl-2-propanone. This last azidoketone is not very stable and must be stored in a refrigerator.

3-azido-4-phenyl-2-butanone 1 : TLC : R_f (Pentane/Ether 90/10) : 0.64. GC : Carbowax column, oven temperature : 190°C. Retention time : 470 s. ^1H NMR (400.13 MHz) δ : 2.18 (s, 3H); AB spectrum δ_{4b} = 2.94 (dd, 1H, J_{4b-4a} = 14.5 Hz, J_{4b-3} = 8.6 Hz); δ_{4a} = 3.17 (dd, 1H, J_{4a-4b} = 14.5 Hz, J_{4a-3} = 5 Hz); 4.05 (dd, 1H, J_{3-4a} = 5 Hz, J_{3-4b} = 8.6 Hz); 7.20-7.38 (m, 5Hz). ^{13}C NMR (100.61 MHz) δ : 27.7 (C-1); 37.2 (C-4); 69.7 (C-3); 127.4 (C-8); 128.9, 129.3 (C-6, C-7); 136.0 (C-5); 205.0 (C-2). Anal. Calcd for $C_{10}H_{11}ON_3$: C : 56.14; H : 9.94; N : 24.56. Found : C : 56.18; H : 9.89; N : 24.63.

1-azido-1-phenyl-2-propanone 2 : TLC : R_f (Pentane/Ether 70/30) : 0.45. GC : Carbowax column, oven temperature : 170°C. Retention time : 330 s. ^1H NMR (400.13 MHz) δ : 2.10 (s, 3H); 5.01 (s, 1H); 7.20-7.55 (m, 5H). ^{13}C NMR (100.61 MHz) δ : 28.7 (C-3); 70.1 (C-1); 126.4 (C-4'); 127.6, 129.5 (C-2', C-3'); 133.8 (C-1'); 202.3 (C-2). Anal. Calcd for $C_9H_9ON_3$: C : 61.70; H : 5.18; N : 23.98. Found : C : 61.70; H : 5.22; N : 23.80.

3 - MICROBIOLOGICAL REDUCTION OF 3-AZIDO-4-PHENYL-2-BUTANONE 1

The incubation times varied and are indicated for each microorganism. The products of the residue were separated on a silica gel column, the eluant was pentane/ether 90/10. The yields given are overall yields for diastereoisomers after work-up. GC analysis was carried out with a Carbowax column, oven temperature : 190°C. The enantiomeric excesses were determined, after reaction of the azidoalcohol with (S)-O-acetyllactyl chloride, by using a Carbowax column, oven temperature : 185°C.

Bakers' yeast : Incubation time : 24 h. The residue from seven flasks consisted of : 55 % (+)-(2S,3S)-3-azido-4-phenyl-2-butanol and 45 % (+)-(2S,3R)-3-azido-4-phenyl-2-butanol. Yield : 72 %.

(+)-(2S,3S)-3-azido-4-phenyl-2-butanol (0.140 g). TLC : R_f (Pentane/Ether 70/30) : 0.37. GC : Retention time : 515 s. ^1H NMR (400.13 MHz) δ : 1.31 (d, 3H, J_{1-2} = 6.5 Hz); 2.50 (s, 1H, exchangeable with D_2O); AB spectrum δ_{4b} = 2.91 (dd, 1H, J_{4b-4a} = 14 Hz, J_{4b-3} = 9 Hz); δ_{4a} = 3.05 (dd, 1H, J_{4a-4b} = 14 Hz, J_{4a-3} = 5.5 Hz); 3.45 (ddd, 1H, J_{3-2} = 4.5 Hz, J_{3-4a} = 5.5 Hz, J_{3-4b} = 9 Hz); 3.79 (td, 1H, J_{2-3} = 4.5 Hz, J_{2-1} = 6.5 Hz); 7.20-7.40 (m, 5H). ^{13}C NMR (100.61 MHz) δ : 20.3 (C-1); 37.1 (C-4); 68.7 (C-3); 69.4 (C-2); 126.8 (C-8); 128.6 ; 129.3 (C-6, C-7); 137.4 (C-5). $[\alpha]_J^{25}$ = + 4 (c = 0.02, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_{10}H_{13}ON_3$: C : 62.81; H : 6.85; N : 21.97. Found : C : 62.72; H : 6.82; N : 21.99.

(+)-(2S,3R)-3-azido-4-phenyl-2-butanol (0.115 g). TLC : R_f (Pentane/Ether 70/30) : 0.34. GC : Retention time : 575 s. ^1H NMR (400.13 MHz) δ : 1.30 (d, 3H, J_{1-2} = 6 Hz); 2.35 (s, 1H, exchangeable with D_2O); AB spectrum δ_{4b} = 2.75 (dd, 1H, J_{4b-4a} = 14 Hz, J_{4b-3} = 9.5 Hz); δ_{4a} = 2.92 (dd, 1H, J_{4a-4b} = 14 Hz, J_{4a-3} = 4.5 Hz); 3.66 (ddd, 1H, J_{3-2} = 4.6 Hz, J_{3-4a} = 4.5 Hz, J_{3-4b} = 9.5 Hz); 3.89 (td, 1H, J_{2-3} = 4.6 Hz, J_{2-1} = 6 Hz); 7.20-7.40 (m, 5H). ^{13}C NMR (100.61 MHz) δ : 18.4 (C-1); 36.6 (C-4); 69.4 (C-3); 69.5 (C-2); 126.8 (C-8); 128.7 ; 129.2 (C-6, C-7); 137.7 (C-5). $[\alpha]_J^{25}$ = + 16 (c = 0.02, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_{10}H_{13}ON_3$: C : 62.81; H : 6.85; N : 21.97. Found : C : 63.20; H : 6.75; N : 21.87.

Mortierella isabellina : Incubation time : 24 h. The residue from eight flasks consisted of : 55 % (+)-(2S,3S)-3-azido-4-phenyl-2-butanol and 45 % (+)-(2S,3R)-3-azido-4-phenyl-2-butanol. Yield : 75 %.

(+)-(2S,3S)-3-azido-4-phenyl-2-butanol (0.165 g). $[\alpha]_J^{25}$ = + 4 (c = 0.02, $CHCl_3$); ee ≥ 98 %.

(+)-(2S,3R)-3-azido-4-phenyl-2-butanol (0.135 g). $[\alpha]_J^{25}$ = + 15 (c = 0.02, $CHCl_3$); ee = 98 %.

Rhodotorula glutinis : Incubation time : 24 h. The residue from six flasks consisted of : 45 % (+)-(2S,3S)-3-azido-4-phenyl-2-butanol and 55 % (+)-(2S,3R)-3-azido-4-phenyl-2-butanol. Yield : 95 %.

(+)-(2S,3S)-3-azido-4-phenyl-2-butanol (0.130 g). $[\alpha]_J^{25}$ = + 4 (c = 0.02, $CHCl_3$); ee ≥ 98 %.
(+)-(2S,3R)-3-azido-4-phenyl-2-butanol (0.145 g). $[\alpha]_J^{25}$ = + 16 (c = 0.03, $CHCl_3$); ee ≥ 98 %.

Beauveria sulfurescens : Incubation time : 48 h. The residue from eight flasks consisted of : 9 % 3-azido-4-phenyl-2-butanone, 28 % (+)-(2S,3S)-3-azido-4-phenyl-2-butanol and 63 % (-)-(2R,3S)-3-azido-4-phenyl-2-butanol. Yield : 60 %.
(+)-(2S,3S)-3-azido-4-phenyl-2-butanol (0.075 g). $[\alpha]_J^{25}$ = + 1 (c = 0.02, $CHCl_3$); ee = 26 %.
(-)-(2R,3S)-3-azido-4-phenyl-2-butanol (0.170 g). $[\alpha]_J^{25}$ = - 2 (c = 0.02, $CHCl_3$); ee = 16 %.

Sporotrichum exile : Incubation time : 24 h. The residue from seven flasks consisted of : 6 % 3-azido-4-phenyl-2-butanone, 27 % (+)-(2S,3S)-3-azido-4-phenyl-2-butanol and 67 % (+)-(2S,3R)-3-azido-4-phenyl-2-butanol. Yield : 60 %.
(+)-(2S,3S)-3-azido-4-phenyl-2-butanol (0.060 g). $[\alpha]_J^{25}$ = + 2 (c = 0.02, $CHCl_3$); ee = 52 %.
(+)-(2S,3R)-3-azido-4-phenyl-2-butanol (0.150 g). $[\alpha]_J^{25}$ = + 14 (c = 0.03, $CHCl_3$); ee = 89 %.

Lactobacillus kefir : Incubation time : 24 h. The residue from six flasks consisted of : 10 % 3-azido-4-phenyl-2-butanone, 40 % (-)-(2R,3R)-3-azido-4-phenyl-2-butanol and 50 % (-)-(2R,3S)-3-azido-4-phenyl-2-butanol. Yield : 75 %.
(-)-(2R,3R)-3-azido-4-phenyl-2-butanol (0.100 g). Same NMR spectra and retention time as those observed for its (2S,3S) enantiomer. $[\alpha]_J^{25}$ = - 4 (c = 0.02, $CHCl_3$); ee ≥ 98 %.
(-)-(2R,3S)-3-azido-4-phenyl-2-butanol (0.125 g). Same NMR spectra and retention time as those observed for its (2S,3R) enantiomer. $[\alpha]_J^{25}$ = - 11 (c = 0.02, $CHCl_3$); ee = 72 %.

Aspergillus niger : Incubation time : 24 h. The residue from ten flasks consisted of : 50 % (-)-(2R,3R)-3-azido-4-phenyl-2-butanol and 50 % (-)-(2R,3S)-3-azido-4-phenyl-2-butanol. Yield : 75 %.
(-)-(2R,3R)-3-azido-4-phenyl-2-butanol (0.190 g). $[\alpha]_J^{25}$ = - 4 (c = 0.03, $CHCl_3$); ee ≥ 98 %.
(-)-(2R,3S)-3-azido-4-phenyl-2-butanol (0.190 g). $[\alpha]_J^{25}$ = - 13 (c = 0.02, $CHCl_3$); ee = 82 %.

Cunninghamella elegans : Incubation time : 48 h. The residue from ten flasks consisted of : 14 % 3-azido-4-phenyl-2-butanone, 39 % (-)-(2R,3R)-3-azido-4-phenyl-2-butanol and 47 % (-)-(2R,3S)-3-azido-4-phenyl-2-butanol. Yield : 50 %.
(-)-(2R,3R)-3-azido-4-phenyl-2-butanol (0.115 g). $[\alpha]_J^{25}$ = - 3 (c = 0.02, $CHCl_3$); ee = 81 %.
(-)-(2R,3S)-3-azido-4-phenyl-2-butanol (0.140 g). $[\alpha]_J^{25}$ = - 11 (c = 0.02, $CHCl_3$); ee = 72 %.

Geotrichum candidum : Incubation time : 24 h. The residue from seven flasks consisted of : 50 % (-)-(2R,3R)-3-azido-4-phenyl-2-butanol and 50 % (-)-(2R,3S)-3-azido-4-phenyl-2-butanol. Yield : 50 %.
(-)-(2R,3R)-3-azido-4-phenyl-2-butanol (0.090 g). $[\alpha]_J^{25}$ = - 4 (c = 0.02, $CHCl_3$); ee ≥ 98 %.
(-)-(2R,3S)-3-azido-4-phenyl-2-butanol (0.090 g). $[\alpha]_J^{25}$ = - 7 (c = 0.02, $CHCl_3$); ee = 45 %.

4 - DETERMINATION OF THE ABSOLUTE CONFIGURATION OF 3-AZIDO-4-PHENYL-2-BUTANOL

The different isomers of 4-phenyl-2,3-epoxybutane were synthesized as previously described[2].

General case : In a 15 mL round-bottom flask, 1.15 mmol. (170 mg) of 4-phenyl-2,3-epoxybutane, 5 eq. (370 mg) of NaN_3 and 2.2 eq. (133 mg) of NH_4Cl were dissolved in 9 mL of a 1/8 mixture water/ methanol. The reaction mixture was refluxed overnight. After evaporation of methanol under vacuum, the residue was diluted with water and extracted several times with ether. The organic phase was dried on $MgSO_4$. After evaporation of ether, the residue was analyzed by GC.

a - From (-)-(2S,3R)-4-phenyl-2,3-epoxybutane

The residue contained 63 % 2-azido-4-phenyl-3-butanol and 37 % 3-azido-4-phenyl-2-butanol. The azidoalcohols were purified on a silica gel column, eluant pentane/ether 90/10. Overall yield : 96 %.

(+)-(2S,3S)-3-azido-4-phenyl-2-butanol (0.080 g). NMR spectra and retention time were identical to those observed for (2S,3S)-3-azido-4-phenyl-2-butanol obtained by microbiological reduction. $[\alpha]_J^{25}$ = + 4 (c = 0.02, $CHCl_3$); ee ≥ 98 %.

(-)-(2R,3R)-2-azido-4-phenyl-3-butanol (0.135 g). TLC : R_f (Pentane/Ether 70/30) : 0.45. GC : Carbowax column, oven temperature : 150°C. Retention time : 1585 s. ^1H NMR (400.13 MHz) δ : 1.38 (d, 3H, J_{1-2} = 7 Hz); 1.95 (s, 1H, exchangeable with D_2O); AB spectrum δ_{4b} = 2.82 (dd, 1H, J_{4b-4a} = 13.7 Hz, J_{4b-3} = 8.1 Hz); δ_{4a} = 2.87 (dd, 1H, J_{4a-4b} = 13.7 Hz, J_{4a-3} = 5.2 Hz); 3.43-3.53 (m, 1H); 3.71 (ddd, 1H, J_{3-4a} = 5.2 Hz, J_{3-4b} = 8.1 Hz, J_{3-2} = 5 Hz); 7.20-7.40 (m, 5H). ^{13}C NMR (100.61 MHz) δ : 15.8 (C-1); 40.5 (C-4); 60.5 (C-2); 75.6 (C-3); 126.7 (C-8); 128.7; 129.4 (C-6, C-7); 137.6 (C-5). $[\alpha]_J^{25}$ = - 45 (c = 0.04, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_{10}H_{13}ON_3$: C : 62.81; H : 6.85; N : 21.97. Found : C : 63.00; H : 6.78; N : 21.89.

b - From (-)-(2S,3S)-4-phenyl-2,3-epoxybutane

The residue contained 80 % 2-azido-4-phenyl-3-butanol and 20 % 3-azido-4-phenyl-2-butanol. The azidoalcohols were purified on a silica gel column, eluant pentane/ether 90/10. Overall yield : 92 %.

(+)-(2S,3R)-3-azido-4-phenyl-2-butanol (0.040 g). NMR spectra and retention time were identical to those observed for (2S,3R)-3-azido-4-phenyl-2-butanol obtained by microbiological reduction. $[\alpha]_J^{25}$ = + 16 (c = 0.02, $CHCl_3$); ee ≥ 98 %.

(-)-(2R,3S)-2-azido-4-phenyl-3-butanol (0.200 g). TLC : R_f (Pentane/Ether 70/30) : 0.43. GC : Carbowax column, oven temperature : 150°C. Retention time : 1100 s. ^1H NMR (400.13 MHz) δ : 1.35 (d, 3H, J_{1-2} = 7 Hz); 2.05 (s, 1H, exchangeable with D_2O); AB spectrum δ_{4b} = 2.72 (dd, 1H, J_{4b-4a} = 13.8 Hz, J_{4b-3} = 9 Hz); δ_{4a} = 2.89 (dd, 1H, J_{4a-4b} = 13.8 Hz, J_{4a-3} = 4.1 Hz); 3.48-3.60 (m, 1H); 3.82 (qu, 1H, J_{3-2} = 4.6 Hz); 7.20-7.40 (m, 5H). ^{13}C NMR (100.61 MHz) δ : 13.9 (C-1); 39.3 (C-4); 60.9 (C-2); 74.9 (C-3); 126.7 (C-8); 128.7; 129.3 (C-6, C-7); 137.7 (C-5). $[\alpha]_J^{25}$ = - 61 (c = 0.03, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_{10}H_{13}ON_3$: C : 62.81; H : 6.85; N : 21.97. Found : C : 62.90; H : 6.82; N : 21.87.

5 - MICROBIOLOGICAL REDUCTION OF 1-AZIDO-1-PHENYL-2-PROPANONE 2

Incubation time was 24 hours. The products of the residue were separated on a silica gel column, the eluant was pentane/ether 90/10. The yields given are overall yields for the diastereoisomers after work-up. GC analysis was carried out with a Carbowax column, oven temperature : 170°C. The enantiomeric excesses were determined on a chiral column (Lipodex E), oven temperature : 110°C for the *syn* isomers and 120°C for the *anti* isomers.

Bakers' yeast : The residue from seven flasks consisted of : 20 % 1-azido-1-phenyl-2-propanone, 10 % (+)-(1S,2S)-1-azido-1-phenyl-2-propanol and 70 % (-)-(1R,2S)-1-azido-1-phenyl-2-propanol. Yield : 60 %.

(+)-(1S,2S)-1-azido-1-phenyl-2-propanol (0.025 g). TLC : R_f (Pentane/Ether 70/30) : 0.25. GC : Retention time : 540 s. ^1H NMR (400.13 MHz) δ : 1.07 (d, 3H, J_{3-2} = 7.5 Hz); 2.48 (s, 1H, exchangeable with D_2O); 3.70 (qu, 1H, J_{1-2} = 7 Hz); 4.48 (d, 1H, J = 8.5 Hz); 7.30-7.50 (m, 5H). ^{13}C NMR (100.61 MHz) δ : 19.2 (C-3); 70.9 ; 73.4 (C-1, C-2); 127.8 (C-4'); 128.9 ; 129.0 (C-2', C-3'); 136.7 (C-1'). $[\alpha]_J^{25}$ = + 250 (c = 0.02, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_9H_{11}ON_3$: C : 61.35; H : 5.72; N : 23.85. Found : C : 61.37; H : 6.00; N : 23.88.

(-)-(1R,2S)-1-azido-1-phenyl-2-propanol (0.185 g). TLC : R_f (Pentane/Ether 70/30) : 0.21. GC : Retention time : 600 s. ^1H NMR (400.13 MHz) δ : 1.20 (d, 3H, J_{3-2} = 7 Hz); 1.78 (s, 1H, exchangeable with D_2O); 3.92-4.04 (m, 1H); 4.49 (d, 1H, J_{1-2}= 7 Hz); 7.30-7.45 (m, 5H). ^{13}C NMR (100.61 MHz) δ : 18.7 (C-3); 70.6; 71.6 (C-1, C-2); 127.9 (C-4'); 128.7; 128.9 (C-2', C-3'); 136.3 (C-1'). $[\alpha]_J^{25}$ = - 206 (c = 0.02, $CHCl_3$); ee ≥ 98 %.

Anal. Calcd for $C_9H_{11}ON_3$: C : 61.35; H : 5.72; N : 23.85. Found : C : 61.38; H : 5.83; N : 23.92.

Mortierella isabellina : The residue from seven flasks consisted of : 40 % (+)-(1S,2S)-1-azido-1-phenyl-2-propanol and 60 % (-)-(1R,2S)-1-azido-1-phenyl-2-propanol. Yield : 90 %.

(+)-(1S,2S)-1-azido-1-phenyl-2-propanol (0.125 g). $[\alpha]_J^{25}$ = + 250 (c = 0.02, $CHCl_3$); ee ≥ 98 %.

(-)-(1R,2S)-1-azido-1-phenyl-2-propanol (0.190 g). $[\alpha]_J^{25}$ = - 206 (c = 0.03, $CHCl_3$); ee ≥ 98 %.

Beauveria sulfurescens : The residue from six flasks consisted of : 10 % 1-azido-1-phenyl-2-propanone, 14 % (+)-(1S,2S)-1-azido-1-phenyl-2-propanol and 76 % (-)-(1R,2S)-1-azido-1-phenyl-2-propanol. Yield : 40 %.

(+)-(1S,2S)-1-azido-1-phenyl-2-propanol (0.020 g). $[\alpha]_J^{25}$ = + 250 (c = 0.01, $CHCl_3$); ee ≥ 98 %.

(-)-(1R,2S)-1-azido-1-phenyl-2-propanol (0.100 g). $[\alpha]_J^{25}$ = - 202 (c = 0.02, $CHCl_3$); ee = 98 %.

Rhodotorula glutinis : The residue from six flasks consisted of : 43 % (+)-(1S,2S)-1-azido-1-phenyl-2-propanol and 57 % (-)-(1R,2S)-1-azido-1-phenyl-2-propanol. Yield : 95 %.

(+)-(1S,2S)-1-azido-1-phenyl-2-propanol (0.125 g). $[\alpha]_J^{25}$ = + 250 (c = 0.04, $CHCl_3$); ee ≥ 98 %.

(-)-(1R,2S)-1-azido-1-phenyl-2-propanol (0.160 g). $[\alpha]_J^{25}$ = - 206 (c = 0.04, $CHCl_3$); ee ≥ 98 %.

Aspergillus niger : The residue from seven flasks consisted of : 40 % 1-azido-1-phenyl-2-propanone, 30 % (+)-(1S,2S)-1-azido-1-phenyl-2-propanol and 30 % (-)-(1R,2S)-1-azido-1-phenyl-2-propanol. Yield : 40 %.

(+)-(1S,2S)-1-azido-1-phenyl-2-propanol (0.070 g). $[\alpha]_J^{25}$ = + 195 (c = 0.02, $CHCl_3$); ee = 78 %.

(-)-(1R,2S)-1-azido-1-phenyl-2-propanol (0.070 g). $[\alpha]_J^{25}$ = - 121 (c = 0.01, $CHCl_3$); ee = 59 %.

Geotrichum candidum : The residue from seven flasks consisted of : 42 % (+)-(1S,2S)-1-azido-1-phenyl-2-propanol and 58 % (-)-(1R,2S)-1-azido-1-phenyl-2-propanol. Yield : 90 %.

(+)-(1S,2S)-1-azido-1-phenyl-2-propanol (0.130 g). $[\alpha]_J^{25}$ = + 200 (c = 0.04, $CHCl_3$); ee = 80 %.

(-)-(1R,2S)-1-azido-1-phenyl-2-propanol (0.185 g). $[\alpha]_J^{25}$ = - 164 (c = 0.01, $CHCl_3$); ee = 80 %.

Lactobacillus kefir : The residue from seven flasks consisted of : 15 % 1-azido-1-phenyl-2-propanone, 47 % (-)-(1R,2R)-1-azido-1-phenyl-2-propanol and 38 % (+)-(1S,2R)-1-azido-1-phenyl-2-propanol. Yield : 85 %.

(-)-(1R,2R)-1-azido-1-phenyl-2-propanol (0.165 g). Same NMR spectra and retention time as those observed for its (1S,2S) enantiomer. $[\alpha]_J^{25}$ = - 175 (c = 0.02, $CHCl_3$); ee = 70 %.

(+)-(1S,2R)-1-azido-1-phenyl-2-propanol (0.130 g). Same NMR spectra and retention time as those observed for its (1R,2S) enantiomer. $[\alpha]_J^{25}$ = + 52 (c = 0.02, $CHCl_3$); ee = 24 %.

6 - SYNTHESES OF AZIDOALCOHOLS FROM 1-PHENYL-1,2-PROPANEDIOL

1-Phenyl-1,2-propanedione is a commercial product (Aldrich).

a - From (1R,2S)-1-phenyl-1,2-propanediol

(-)-(1R,2S)-1-phenyl-1,2-propanediol was prepared by the microbiological reduction of 1-phenyl-1,2-propanedione with bakers' yeast according to the method described previously[9].

To 0.500 g of (-)-(1R,2S)-1-phenyl-1,2-propanediol dissolved in 6 mL of CCl_4 was added 0.4 mL of thionyl chloride. The mixture was refluxed for 0.5 hour. After cooling, it was diluted with ether and the organic phase was washed with saturated aqueous $NaHCO_3$ and dried on $MgSO_4$. After evaporation of the solvent, we obtained 0.500 g of the cyclic sulfite, which was used directly in the second step of the reaction.

To 0.500 g of the cyclic sulfite dissolved in 25 mL of dimethylformamide was added 0.35 g of lithium azide. The mixture was stirred and heated at 115-120°C overnight. After cooling, the mixture was diluted with 30 mL of water and extracted three times with ether. The organic phase was washed with saturated $NaHCO_3$ solution and dried on $MgSO_4$. After evaporation of the ether, the residue was analyzed by GC : it contained 58 % 1-azido-1-phenyl-2-propanol and 42 % 2-azido-1-phenyl-1-propanol. The azidoalcohols were purified on a silica gel column, eluant Pentane/Ether 90/10. Overall yield : 78 %.

(+)-(1S,2S)-1-azido-1-phenyl-2-propanol (0.265 g). NMR spectra and retention time were identical to those observed with (1S,2S)-1-azido-1-phenyl-2-propanol obtained by microbiological reduction. $[\alpha]_J^{25} = + 250$ (c = 0.02, $CHCl_3$); ee ≥ 98 %.

(-)-(1R,2R)-2-azido-1-phenyl-1-propanol (0.190 g). TLC : R_f (Pentane/Ether 90/10) : 0.19. GC : Carbowax column, oven temperature : 170°C. Retention time : 910 s. ^1H NMR (400.13 MHz) δ : 1.12 (d, 3H, $J_{3-2} = 7$ Hz); 2.50 (s, 1H, exchangeable with D_2O); 3.68 (qu, 1H, J = 7 Hz); 4.48 (d, 1H, $J_{1-2} = 7.5$ Hz); 7.30-7.40 (m, 5H). ^{13}C NMR (100.61 MHz) δ : 15.9 (C-3); 63.5 (C-2); 78.1 (C-1); 126.8; 128.4; 128.6 (C-2', C-3', C-4'); 140.4 (C-1'). $[\alpha]_J^{25} = - 140$ (c = 0.03, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_9H_{11}ON_3$: C : 61.35; H : 5.72; N : 23.85. Found : C : 61.29; H : 5.80; N : 23.92.

b - From (1S,2S)-1-phenyl-1,2-propanediol

(+)-(1S,2S)-1-phenyl-1,2-propanediol was prepared by the microbiological reduction of 1-phenyl-1,2-propanedione with *Beauveria sulfurescens* as previously described[8].

The corresponding cyclic sulfite was prepared using the same procedure as above from 0.130 g of (1S,2S)-1-phenyl-1,2-propanediol. We obtained, after treatment with lithium azide and work-up, a mixture of 90 % 1-azido-1-phenyl-2-propanol and 10 % of 2-azido-1-phenyl-1-propanol. The azidoalcohols were purified as above. Overall yield : 75 %.

(-)-(1R,2S)-1-azido-1-phenyl-2-propanol (0.100 g). NMR spectra and retention time were identical to those observed with (1R,2S)-1-azido-1-phenyl-2-propanol obtained by microbiological reduction. $[\alpha]_J^{25} = - 206$ (c = 0.02, $CHCl_3$); ee ≥ 98 %.

(-)-(1S,2R)-2-azido-1-phenyl-1-propanol (0.010 g). TLC : R_f (Pentane/Ether 90/10) : 0.20. GC : Carbowax column, oven temperature : 170°C. Retention time : 910 s. ^1H NMR (400.13 MHz) δ : 1.21 (d, 3H, $J_{3-2} = 6$ Hz); 1.60 (s, 1H, exchangeable with D_2O); 3.75 (qd, 1H, $J_{2-3} = 6$ Hz, $J_{2-1} = 4.5$ Hz); 4.76 (dd, 1H, $J_{1-2} = 4.5$ Hz, $J_{1-OH} = 2$ Hz); 7.30-7.45 (m, 5H). ^{13}C NMR (100.61 MHz) δ : 13.6 (C-3); 62.5 (C-2); 76.5 (C-1); 126.5; 128.2; 128.6 (C-2', C-3', C-4'); 140.2 (C-1'). $[\alpha]_J^{25} = - 50$ (c = 0.01, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_9H_{11}ON_3$: C : 61.35; H : 5.72; N : 23.85. Found : C : 61.40; H : 5.75; N : 23.78.

7 - PREPARATION OF HOMOCHIRAL AMINOALCOHOLS.

General Method : To a solution of 0.26 mmol. of $LiAlH_4$ in 10 mL of anhydrous ether was added dropwise a solution of 0.52 mmol. of azidoalcohol in 5 mL of anhydrous ether. The mixture was refluxed for three hours. After cooling, 5 mL of water was added carefully, and the mixture was extracted three times with ether. The organic phase was washed with brine and dried on $MgSO_4$. The solvent was evaporated under vacuum, yielding the pure aminoalcohol.

a - From 3-azido-2-octanol

- From 0.050 g of (+)-(2S,3S)-3-azido-2-octanol obtained by microbiological reduction with *Beauveria sulfurescens*, 0.040 g of (-)-(2S,3S)-3-amino-2-octanol was prepared. Yield : 93 %.

(-)-(2S,3S)-3-amino-2-octanol. Colorless liquid, crystallizes in the refrigerator. TLC : R_f (Pentane/Ether 70/30) : 0.05. ^1H NMR (300.13 MHz) δ: 0.90 (t, 3H, J_{1-2} = 5 Hz); 1.16 (d, 3H, J_{8-7} = 6 Hz); 1.22-1.40 (m, 6H); 1.41-1.60 (m, 2H); 2.14 (s, 3H, exchangeable with D_2O); 2.40-2.48 (m, 1H); 3.40 (qu, 1H, J = 6 Hz). ^{13}C NMR (75.47 MHz) δ: 14.0 (C-8); 20.2 (C-1); 22.6 (C-7); 25.9 (C-6); 31.9 (C-5); 34.3 (C-4); 57.5 (C-3); 70.3 (C-2). $[\alpha]_J^{25}$ = - 11 (c = 0.03, $CHCl_3$); ee = 97 %. Anal. Calcd for $C_8H_{19}ON$: C : 66.16; H : 13.18; N : 9.65. Found : C : 66.33; H : 13.31; N : 9.41.

- From 0.090 g of (-)-(2R,3R)-3-azido-2-octanol obtained by microbiological reduction with *Lactobacillus kefir*, 0.070 g of (+)-(2R,3R)-3-amino-2-octanol was prepared. Yield : 90 %.

(+)-(2R,3R)-3-amino-2-octanol.Same NMR spectra as observed for those of its (2S,3S) enantiomer. $[\alpha]_J^{25}$ = + 11 (c = 0.01, $CHCl_3$); ee = 97 %

- From 0.050 g of (+)-(2S,3R)-3-azido-2-octanol obtained by microbiological reduction with bakers' yeast, 0.040 g of (+)-(2S,3R)-3-amino-2-octanol was prepared. Yield : 93 %.

(+)-(2S,3R)-3-amino-2-octanol. Colorless oil. TLC : R_f (Pentane/Ether 70/30) : 0.05. ^1H NMR (300.13 MHz) δ : 0.88 (t, 3H, J_{8-7} = 6 Hz); 1.10 (d, 3H, J_{1-2} = 6 Hz); 1.12-1.36 (m, 6H); 1.36-1.50 (m, 2H); 2.00 (s, 3H, exchangeable with D_2O); 2.70-2.84 (m, 1H); 3.67-3.85 (m, 1H). ^{13}C NMR (75.47 MHz) δ: 14.0 (C-8); 16.9 (C-1); 22.6 (C-7); 26.3 (C-6); 32.0 (C-5); 33.0 (C-4); 56.0 (C-3); 69.9 (C-2). $[\alpha]_J^{25}$ = + 3 (c = 0.03, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_8H_{19}ON$: C : 66.16; H : 13.18; N : 9.65. Found : C : 65.83; H : 13.29; N : 9.81.

- From 0.050 g of (-)-(2R,3S)-3-azido-2-octanol obtained by microbiological reduction with *Lactobacillus kefir*, 0.040 g of (-)-(2R,3S)-3-amino-2-octanol was prepared. Yield : 90 %.

(-)-(2R,3S)-3-amino-2-octanol. Same NMR spectra as observed for those of its (2S,3R) enantiomer. $[\alpha]_J^{25}$ = - 3 (c = 0.04, $CHCl_3$); ee ≥ 98 %.

b - From 2-azido-3-octanol

- From 0.050 g of (-)-(2R,3R)-2-azido-3-octanol obtained by the opening of the cyclic sulfite, 0.040 g of (+)-(2R,3R)-2-amino-3-octanol was prepared. Yield : 95 %.

(+)-(2R,3R)-2-amino-3-octanol. White solid. F = 52-54°C. TLC : R_f (Pentane/Ether 70/30) : 0.045. ^1H NMR (300.13 MHz) δ : 0.88 (t, 3H, J_{8-7} = 7 Hz); 1.07 (d, 3H, J_{1-2} = 7 Hz); 1.15-1.38 (m, 6H); 1.41-1.55 (m, 2H); 2.60-2.83 (m, 4H, 3H exchangeable with D_2O); 3.09-3.21 (m, 1H). ^{13}C NMR (75.47 MHz) δ: 14.0 (C-8); 20.6 (C-1); 22.7 (C-7); 25.5 (C-6); 32.0 (C-5); 34.2 (C-4); 51.3 (C-2); 75.6 (C-3). $[\alpha]_J^{25}$ = + 14 (c = 0.04, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_8H_{19}ON$: C : 66.16; H : 13.18; N : 9.65. Found : C : 66.31; H : 13.00; N : 9.58.

- From 0.070 g of (-)-(2R,3S)-2-azido-3-octanol obtained by the opening of the cyclic sulfite, 0.055 g of (-)-(2R,3S)-2-amino-3-octanol was prepared. Yield : 93 %.

(-)-(2R,3S)-2-amino-3-octanol. Yellow oil. TLC : R_f (Pentane/Ether 70/30) : 0.045. ^1H NMR (300.13 MHz) δ : 0.90 (t, 3H, J_{8-7} = 5 Hz); 1.01 (d, 3H, J_{1-2} = 7 Hz); 1.26-1.42 (m, 6H); 1.45-1.60 (m, 2H); 1.98 (s, 3H, exchangeable with D_2O); 2.90-3.00 (m, 1H); 3.38-3.48 (m, 1H). ^{13}C NMR (75.47 MHz) δ: 14.0 (C-8 ; 17.0 (C-1); 22.6 (C-7); 25.9 (C-6); 32.0 (C-5); 32.5 (C-4); 50.5 (C-2); 74,8 (C-3). $[\alpha]_J^{25}$ = - 16 (c = 0.05, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_8H_{19}ON$: C : 66.16; H : 13.18; N : 9.65. Found : C : 66.19; H : 13.30; N : 9.72.

c - From 3-azido-4-phenyl-2-butanol

- From 0.050 g of (+)-(2S,3S)-3-azido-4-phenyl-2-butanol obtained by microbiological reduction with bakers' yeast, 0.040 g of (-)-(2S,3S)-3-amino-4-phenyl-2-butanol was prepared. Yield : 88 %.

(-)-(2S,3S)-3-amino-4-phenyl-2-butanol. Liquid. TLC : R_f (Pentane/Ether 70/30) : 0.04. ^1H NMR (400.13 MHz) δ : 1.30 (d, 3H, J_{1-2} = 7 Hz); 1.90 (s, 3H, exchangeable with D_2O); AB spectrum δ_{4b} = 2.43 (dd, 1H,

J_{4b-4a} = 13.5 Hz, J_{4b-3} = 9.9 Hz); δ_{4a} = 2.95 (dd, 1H, J_{4a-4b} = 13.5 Hz, J_{4a-3} = 4.1 Hz); 2.74-2.84 (m, 1H); 3.55 (qu, 1H, J = 6.2 Hz); 7.15-7.38 (m, 5H). ^{13}C NMR (100.61 MHz) δ: 20.5 (C-1); 41.0 (C-4); 58.6 (C-3); 69.9 (C-2); 126.5 (C-8); 128.7; 129.3 (C-6, C-7); 139.1 (C-5). $[\alpha]_J^{25}$ = - 27 (c = 0.03, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_{10}H_{15}ON$: C : 72.69; H : 9.15; N : 8.48. Found : C : 72.71; H : 9.18; N : 8.58.

- From 0.070 g of (-)-(2R,3R)-3-azido-4-phenyl-2-butanol obtained by microbiological reduction with *Aspergillus niger*, 0.050 g of (+)-(2R,3R)-3-amino-4-phenyl-2-butanol was prepared. Yield : 85 %.
(+)-(2R,3R)-3-amino-4-phenyl-2-butanol. Same NMR spectra as observed for its (2S,3S) enantiomer. $[\alpha]_J^{25}$ = + 27 (c = 0.03, $CHCl_3$); ee ≥ 98 %.

- From 0.050 g of (+)-(2S,3R)-3-azido-4-phenyl-2-butanol obtained by microbiological reduction with *Rhodotorula glutinis*, 0.035 g of (+)-(2S,3R)-3-amino-4-phenyl-2-butanol was prepared. Yield : 85 %.
(+)-(2S,3R)-3-amino-4-phenyl-2-butanol. Liquid. TLC : R_f (Pentane/Ether 70/30) : 0.04. ^1H NMR (400.13 MHz) δ : 1.23 (d, 3H, J_{1-2} = 7 Hz); 1.70 (s, 3H, exchangeable with D_2O); AB spectrum δ_{4b} = 2.45 (dd, 1H, J_{4b-4a} = 13.6 Hz, J_{4b-3} = 10.5 Hz); δ_{4a} = 2.87 (dd, 1H, J_{4a-4b} = 13.6 Hz, J_{4a-3} = 3.8 Hz); 3.00-3.11 (m, 1H); 3.74-3.83 (m, 1H); 7.15-7.37 (m, 5H). ^{13}C NMR (100.61 MHz) δ: 17.7 (C-1); 38.5 (C-4); 57.5 (C-3); 69.8 (C-2); 126.4 (C-8); 128.6; 129.2 (C-6, C-7); 139.4 (C-5). $[\alpha]_J^{25}$ = + 35 (c = 0.03, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_{10}H_{15}ON$: C : 72.69; H : 9.15; N : 8.48. Found : C : 72.80; H : 8.82; N : 8.58.

- From 0.080 g of (-)-(2R,3S)-3-azido-4-phenyl-2-butanol obtained by microbiological reduction with *Aspergillus niger*, 0.060 g of (-)-(2R,3S)-3-amino-4-phenyl-2-butanol was prepared. Yield : 88 %.
(-)-(2R,3S)-3-amino-4-phenyl-2-butanol. Same NMR spectra as observed for those of its (2S,3S) enantiomer. $[\alpha]_J^{25}$ = - 29 (c = 0.03, $CHCl_3$); ee = 82 %.

d - From 2-azido-4-phenyl-3-butanol

- From 0.050 g of (-)-(2R,3R)-2-azido-4-phenyl-3-butanol obtained by the opening of (2S,3R)-4-phenyl-2,3-epoxybutane, 0.039 g of (+)-(2R,3R)-2-amino-4-phenyl-3-butanol was prepared. Yield : 90 %.
(+)-(2R,3R)-2-amino-4-phenyl-3-butanol. White solid. F = 62-64°C. ^1H NMR (400.13 MHz) δ : 1.10 (d, 3H, J_{1-2} = 6.2 Hz); 2.20 (s, 3H, exchangeable with D_2O); AB spectrum δ_{4b} = 2.63 (dd, 1H, J_{4b-4a} = 13.7 Hz, J_{4b-3} = 8.5 Hz); δ_{4a} = 2.85 (dd, 1H, J_{4a-4b} = 13.7 Hz, J_{4a-3} = 3.9 Hz); 2.80 (qu, 1H, J = 6.2 Hz); 3.38-3.47 (m, 1H); 7.10-7.40 (m, 5H). ^{13}C NMR (100.61 MHz) δ: 20.7 (C-1); 40.8 (C-4); 50.4 (C-2); 76.5 (C-3); 126.3 (C-8); 128.4; 129.4 (C-6, C-7); 138.9 (C-5). $[\alpha]_J^{25}$ = + 27 (c = 0.03, $CHCl_3$) ee ≥ 98 %. Anal. Calcd for $C_{10}H_{15}ON$: C : 72.69; H : 9.15; N : 8.48. Found : C : 72.63; H : 9.04; N : 8.33.

- From 0.040 g of (-)-(2R,3S)-2-azido-4-phenyl-3-butanol obtained by opening of (2S,3S)-4-phenyl-2,3-epoxybutane, 0.031 g of (-)-(2R,3S)-2-amino-4-phenyl-3-butanol was prepared. Yield : 90 %.
(-)-(2R,3S)-2-amino-4-phenyl-3-butanol. White solid. F = 68-69°C. ^1H NMR (400.13 MHz) δ : 1.10 (d, 3H, J_{1-2} = 7 Hz); 1.96 (s, 3H, exchangeable with D_2O); AB spectrum δ_{4b} = 2.68 (dd, 1H, J_{4b-4a} = 13.5 Hz, J_{4b-3} = 9.2 Hz); δ_{4a} = 2.75 (dd, 1H, J_{4a-4b} = 13.5 Hz, J_{4a-3} = 4.6 Hz); 2.90-3.01 (m, 1H); 3.67 (qu, 1H, J = 4.6 Hz); 7.15-7.38 (m, 5H). ^{13}C NMR (100.61 MHz) δ: 17.4 (C-1); 39.1 (C-4); 50.1 (C-2); 76.0 (C-3); 126.4 (C-8); 128.5; 129.3 (C-6, C-7); 139.0 (C-5). $[\alpha]_J^{25}$ = - 31 (c = 0.03, $CHCl_3$); ee ≥ 98 %. Anal. Calcd for $C_{10}H_{15}ON$: C : 72.69; H : 9.15; N : 8.48. Found : C : 72.66; H : 9.33; N : 8.28.

8 - SYNTHESES OF AZIRIDINES

General Method : 0.58 mmol. of azidoalcohol and 0.58 mmol. (0.150 g) of triphenylphosphine were dissolved in 5 mL of THF. The mixture was heated at 70°C overnight. After cooling, 5 mL of water was added and the mixture was extracted three times with ether. The organic phase was washed with brine and dried on $MgSO_4$.

After evaporation of the solvent, a white solid of triphenylphosphine oxide appeared. After filtration of this solid, the aziridine was purified further by bulb-to-bulb distillation.

a - From 3-azido-2-octanol

Cis and especially *trans* 2-methyl-3-*n*-pentylaziridines are very unstable at room temperature, and they are degraded by an acidic or basic medium. As a result, the optical rotations were measured in pentane. GC analysis was performed on a Carbowax column, oven temperature : 90°C for 5 min, then 90°C to 170°C at 4°C/min and 170°C for 5 min. The temperature of the bulb-to-bulb distillation was 150-200°C for 2-methyl-3-*n*-pentylaziridine.

- From 0.150 g of (+)-(2S,3S)-3-azido-2-octanol obtained by microbiological reduction with *Beauveria sulfurescens*, 0.085 g of (+)-(2R,3S)-2-methyl-3-*n*-pentylaziridine was prepared. Yield : 75 %.

(+)-(2R,3S)-2-methyl-3-*n*-pentylaziridine. Colorless liquid. TLC : R_f (Pentane/Ether 10/90) : 0.1. Retention time : 275 s. ^1H NMR (300.13 MHz) δ : 0.89 (t, 3H, J_{8-7} = 6 Hz); 1.12 (d, 3H, J_{1-2} = 6.5 Hz); 1.20-1.50 (m, 9H, 1H exchangeable with D_2O); 1.90 (q, 1H, J_{2-1} = 6.5 Hz); 2.05 (qu, 1H, J = 6.5 Hz). ^{13}C NMR (75.47 MHz) δ: 14.1 (C-8); 19.4 (C-1); 22.7 (C-7); 27.4 (C-6); 31.7 (C-5); 32.7; 34.3 (C-2, C-3); 38.8 (C-4). $[\alpha]_J^{25}$ = + 1 (c = 0.03, Pentane); ee = 97 %. HRMS : Calculated : 127.2314. Found : 127.2318.

- From 0.090 g of (-)-(2R,3R)-3-azido-2-octanol obtained by microbiological reduction with *Lactobacillus kefir*, 0.050 g of (-)-(2S,3R)-2-methyl-3-*n*-pentylaziridine was prepared. Yield : 73 %.

(-)-(2S,3R)-2-methyl-3-*n*-pentylaziridine. NMR spectra and retention time were identical to those observed with its (2R,3S) enantiomer. $[\alpha]_J^{25}$ = - 1 (c = 0.03, Pentane); ee = 97 %.

- From 0.120 g of (+)-(2S,3R)-3-azido-2-octanol obtained by microbiological reduction with bakers' yeast, 0.040 g of (+)-(2R,3R)-2-methyl-3-*n*-pentylaziridine was prepared. Yield : 65 %.

(+)-(2R,3R)-2-methyl-3-*n*-pentylaziridine. Colorless liquid. TLC : R_f (Pentane/Ether 10/90) : 0.1. Retention time : 230 s. ^1H NMR (300.13 MHz) δ : 0.92 (t, 3H, J_{8-7} = 5 Hz); 1.18 (d, 3H, J_{1-2} = 7 Hz); 1.28-1.40 (m, 9H, 1H exchangeable with D_2O); 1.52-1.65 (m, 1H); 1.65-1.75 (m, 1H). ^{13}C NMR (75.47 MHz) δ: 13.9 (C-8); 14.0 (C-1); 21.4 (C-7); 28.5 (C-6); 28.6 (C-5); 29.4; 27.2 (C-2, C-3); 29.8 (C-4). $[\alpha]_J^{25}$ = + 57 (c = 0.03, Pentane); ee ≥ 98 %. HRMS : Calculated : 127.2314. Found : 127.2316.

- From 0.090 g of (-)-(2R,3S)-3-azido-2-octanol obtained by microbiological reduction with *Lactobacillus kefir*, 0.050 g of (-)-(2S,3S)-2-methyl-3-*n*-pentylaziridine was prepared. Yield : 68 %.

(-)-(2S,3S)-2-methyl-3-*n*-pentylaziridine. NMR spectra and retention time were identical to those observed with its (2R,3R) enantiomer. $[\alpha]_J^{25}$ = - 57 (c = 0.03, Pentane); ee ≥ 98 %.

b - From 3-azido-4-phenyl-2-butanol

The temperature of the bulb-to-bulb distillation was 200°C under 13 mm Hg. GC analysis was performed on a Carbowax column, oven temperature : 120°C.

- From 0.080 g of (+)-(2S,3S)-3-azido-4-phenyl-2-butanol obtained by microbiological reduction with bakers' yeast, 0.045 g of (-)-(2R,3S)-2-methyl-3-benzylaziridine was prepared. Yield : 70 %.

(-)-(2R,3S)-2-methyl-3-benzylaziridine. Colorless liquid. TLC : R_f (Pentane/Ether 70/30) : 0.15. Retention time : 450 s. ^1H NMR (400.13 MHz) δ: 1.25 (d, 3H, J = 5.6 Hz); 1.75 (s, 1H exchangeable with D_2O); 2.20 (qu, 1H, J = 5.6 Hz); 2.25 (q, 1H, J = 6.6 Hz); AB spectrum δ_{4b} = 2.68 (dd, 1H, J_{4b-4a} = 14.8 Hz, J_{4b-3} = 6.6 Hz); δ_{4a} = 2.79 (dd, 1H, J_{4a-4b} = 14.8 Hz, J_{4a-3} = 6.1 Hz); 7.15-7.40 (m, 5H). ^{13}C NMR (100.61 MHz) δ: 14.2 (C-1); 29.9 (C-4); 34.9; 35.8 (C-2, C-3); 126.2 (C-8); 128.5; 128.7 (C-6, C-7); 140.2 (C-5). $[\alpha]_J^{25}$ = - 18 (c =

0.03, Pentane); ee ≥ 98 %. $[\alpha]_J^{25}$ = - 9 (c = 0.03, $CHCl_3$: the product tends to racemize). HRMS : Calculated : 147.1048. Found : 147.1049.

- From 0.100 g of (-)-(2R,3R)-3-azido-4-phenyl-2-butanol obtained by microbiological reduction with *Aspergillus niger*, 0.055 g of (+)-(2S,3R)-2-methyl-3-benzylaziridine was prepared. Yield : 69 %.
(+)-(2S,3R)-2-methyl-3-benzylaziridine. Same NMR spectra and retention time as those observed for its (2R,3S) enantiomer. $[\alpha]_J^{25}$ = + 18 (c = 0.03, Pentane); ee ≥ 98 %.

- From 0.100 g of (+)-(2S,3R)-3-azido-4-phenyl-2-butanol obtained by microbiological reduction with *Rhodotorula glutinis*, 0.060 g of (+)-(2R,3R)-2-methyl-3-benzylaziridine was prepared. Yield : 75 %.
(+)-(2R,3R)-2-methyl-3-benzylaziridine. TLC : R_f (Pentane/Ether 70/30) : 0.15. Retention time : 335 s. ^1H NMR (400.13 MHz) δ : 1.25 (d, 3H, J_{1-2} = 7 Hz); 1.50 (s, 1H exchangeable with D_2O); 1.72-1.84 (m, 1H); 1.84-1.94 (m, 1H); AB spectrum δ_{4b} = 2.69 (dd, 1H, J_{4b-4a} = 14.9 Hz, J_{4b-3} = 6.4 Hz); δ_{4a} = 2.83 (dd, 1H, J_{4a-4b} = 14.9 Hz, J_{4a-3} = 5.7 Hz); 7.10-7.40 (m, 5H). ^{13}C NMR (100.61 MHz) δ: 19.2 (C-1); 32.5 (C-4); 39.0; 39.7 (C-2, C-3); 126.4 (C-8); 128.5; 128.7 (C-6, C-7); 139.0 (C-5). $[\alpha]_J^{25}$ = + 64 (c = 0.04, Pentane); ee ≥ 98 %. $[\alpha]_J^{25}$ = + 93 (c = 0.04, $CHCl_3$: the product tends to racemize). HRMS : Calculated : 147.1048. Found : 147.1048.

- From 0.070 g of (-)-(2R,3S)-3-azido-4-phenyl-2-butanol obtained by microbiological reduction with *Aspergillus niger*, 0.040 g of (-)-(2S,3S)-2-methyl-3-benzylaziridine was prepared. Yield : 70 %.
(-)-(2S,3S)-2-methyl-3-benzylaziridine. Same NMR spectra and retention time as those observed for its (2R,3R) enantiomer. $[\alpha]_J^{25}$ = - 52 (c = 0.02, Pentane); ee = 82 %.

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