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Stereoselective aza-MIRC reactions on optically active (*E*)-nitro alkenes

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Abstract—Optically active (*E*)-nitro alkenes carrying a 1,3-dioxolane or 1,3-oxazolidine residue undergo stereoselective aza-MIRC reactions, leading to the synthesis of the corresponding chiral nitro aziridines in high yields and with good diastereoselectivity. Interestingly, the stereochemical outcome of the aziridination reactions was strongly influenced by the chiral residue considered, giving stereoisomers, regardless of the reaction conditions.

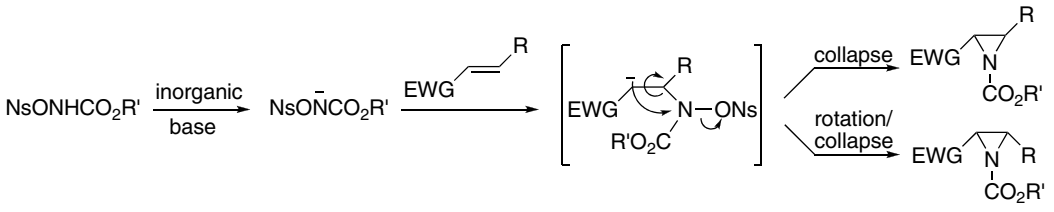
1. Introduction

Aziridines are among the most fascinating intermediates in organic synthesis, acting as precursors to complex molecules due to the strain incorporated in their skeletons.[1] Besides their importance as reactive intermediates, many biologically active compounds also contain these three-membered rings.[2] Thus, obtaining aziridines, especially optically active aziridines, has become of great importance in organic chemistry.

The chemistry of aziridines was hindered by the dearth of suitable methods available: as a synthetic process, aziridination is poorly developed. In particular, the range of direct synthetic methodology available to obtain aziridines starting from alkenes is narrow.[3]

For many years our research group has developed an efficient direct aziridination methodology, which involves the aza-MIRC (Michael initiated ring closure) reaction promoted by inorganic bases on alkyl nosyloxycarbamates ($NsONHCO_2R$, $Ns = 4\text{-}NO_2C_6H_4SO_2$) starting from electron poor alkenes (Scheme 1).[4]

Our interest has been devoted to different alkenes containing different EWGs (electron withdrawing groups), the reaction leading to mixtures of diastereomeric aziridines, in relationship with the substituents considered. The nitro group, which is a strong electron withdrawing group and a well-known precursor of the important amine functionality,[5] promptly caught our attention.[6]



Scheme 1.

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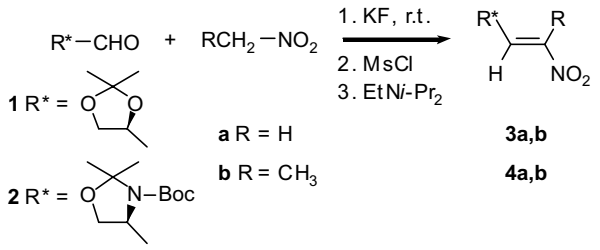
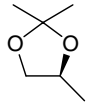
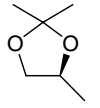
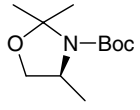
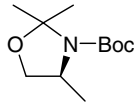
2. Results and discussion

We report herein novel studies in this field, extending our methodology to the synthesis of optically active nitro aziridines by direct amination of nitro alkenes. Starting from commercially available nitro alkanes, we performed a Henry condensation reaction[7] with (*R*)-2,2-dimethyl-1,3-dioxolane-4-carboxaldehyde **1** and with *tert*-butyl (*R*)-4-formyl-2,2-dimethyl-1,3-oxazolidine-3-carboxylate (Garner's aldehyde) **2** (Scheme 2), useful precursors of important chemical functionality.[8] Dehydration reaction of the intermediate nitro aldols gives the expected nitro alkenes **3a**,**b** and **4a**,**b** in the yields reported in Table 1.



Scheme 2.

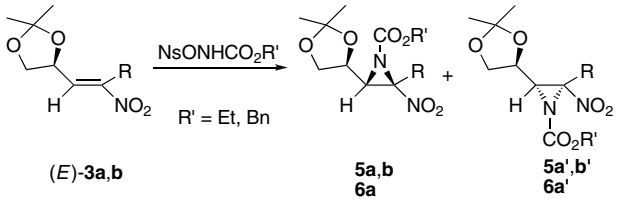
Table 1. Synthesis of nitro alkenes at 0 °C

Alkene	R*	R	Yield (%)	*E*/*Z*
3a		H	77	>99:1
3b		CH_3	75	91:9[a]
4a		H	76	>99:1
4b		CH_3	82	>99:1

[a] *E*-Isomer was purified by flash chromatography.

We found that the dehydration reaction can be stereochemically controlled by changing the temperature. In fact, working under the reported conditions (−78 °C),[7] diastereomeric mixtures 70:30 of *E*/*Z* nitro olefins were obtained: an increase of the reaction temperature (0 °C) allowed us to obtain the single *E*-isomer, except that for **3b**, which was however obtained with satisfactory purity.

The chiral (*E*)-nitro alkenes **3** were aziridinated using different carbamates ($NsONHCO_2Et$ or $NsONHCO_2Bn$) and changing the reaction conditions. In all cases the aziridines were obtained in high yields and with good stereoselectivity (Scheme 3). The results are reported in Table 2.



Scheme 3.

Table 2. Aziridination of (*E*)-nitro alkenes **3**

Entry	Alkene	R′	Solvent	Base	Time (h)	Yield[a] (%)	Aziridine[b] (dr)
1	(*E*)-**3a**	Et	CH_2Cl_2	CaO	4	82	**5a**/**5a**′ (8:2)
2	(*E*)-**3a**	Bn	CH_2Cl_2	CaO	3	85	**6a**/**6a**′ (8:2)
3	(*E*)-**3a**	Et	THF	NaH	1	78	**5a**/**5a**′ (8:2)
4	(*E*)-**3a**	Bn	THF	NaH	1	75	**6a**/**6a**′ (8:2)
5	(*E*)-**3a**	Et	—	CaO	0.5	70	**5a**/**5a**′ (8:2)
6	(*E*)-**3b**	Et	CH_2Cl_2	CaO	4	79	**5b**/**5b**′ (7:3)
7	(*E*)-**3b**	Et	—	CaO	0.5	72	**6b**/**6b**′ (7:3)

[a] After flash chromatography. The isomers could not be separated by HPLC.
[b] Determined by ^1H NMR spectra on crude mixtures.

The aziridination reactions occurred with complete retention of stereochemistry of the substrates, also in solvent-free conditions (entries 5 and 7) and only stereoisomers were obtained. The ^1H NMR spectra performed on the crude mixture showed the presence of diastereomeric aziridines with the same configuration of the starting alkenes, as confirmed by the coupling constant values[9] (Fig. 1).

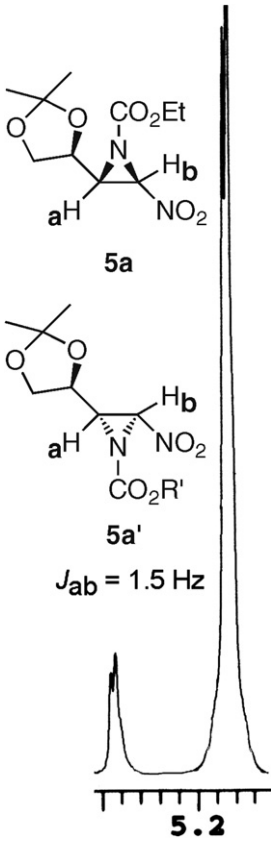
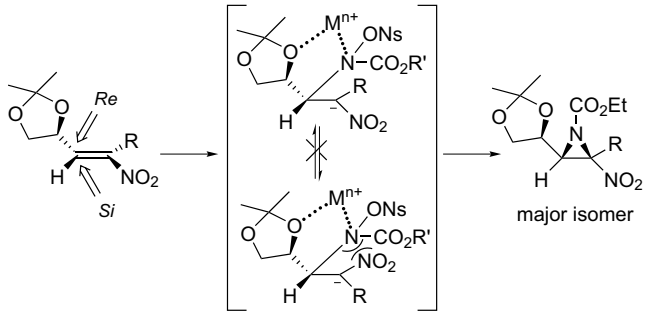


Figure 1.

The stereochemical result can be explained by the involvement of a dioxolane oxygen in the first step of aziridination, as in other related three-membered ring forming reactions.[10] As a result of the coordination of the nucleophilic attack, free rotation around the single bond of the intermediate would be completely inhibited and the major isomer derived by attack on the *Re* face of chiral olefins (Scheme 4).



Scheme 4.

Interestingly, a different stereochemical reaction outcome was observed when *tert*-butyl (*R*)-4-formyl-2,2-dimethyl-1,3-oxazolidine-3-carboxylate was used as a resident chiral residue (Scheme 5).

As reported in Table 3, starting from alkenes **4a**,**b** a very high asymmetric induction leading to the formation of only one of the possible diastereomers of aziridines was observed regardless of the choice of the aminating agent, of the inorganic base, and of the solvent.

Table 3. Aziridination of (*E*)-nitro alkenes **4**

Entry	Alkene	R′	Solvent	Base	Time (h)	Yield[a] (%)	Aziridine[b] (dr)
1	(*E*)-**4a**	Et	CH_2Cl_2	CaO	3.5	81	**7a**/**7a′** (6:4)
2	(*E*)-**4a**	Bn	CH_2Cl_2	CaO	3	84	**8a**/**8a′** (6:4)
3	(*E*)-**4a**	Et	THF	NaH	1	78	**7a**/**7a′** (6:4)
4	(*E*)-**4a**	Bn	THF	NaH	1	79	**8a**/**8a′** (6:4)
5	(*E*)-**4b**	Et	CH_2Cl_2	CaO	4	78	**7b**/**7b′** (7:3)
6	(*E*)-**4b**	Et	—	CaO	0.5	72	**7b**/**7b′** (7:3)

[a] After flash chromatography. The isomers were separated by HPLC.
[b] Determined by ^{1}H NMR spectra on crude mixtures.

The analyses of ^{1}H NMR spectra performed on the crude mixture confirmed the formation of two diastereomers of nitro aziridines, due to the expected free rotation around the single bond of the reaction intermediates.

The aziridine proton b signal in the ^{1}H NMR spectrum of isomer **7a** is doubled probably because of the presence of rotamers, due to the proximity to the Boc group, differently from the proton b signal of isomer **7a′** (Fig. 2). According to the formation of two diastereomers **7a** and **7a′**, the coupling constants for these signals are different (see Section 4).

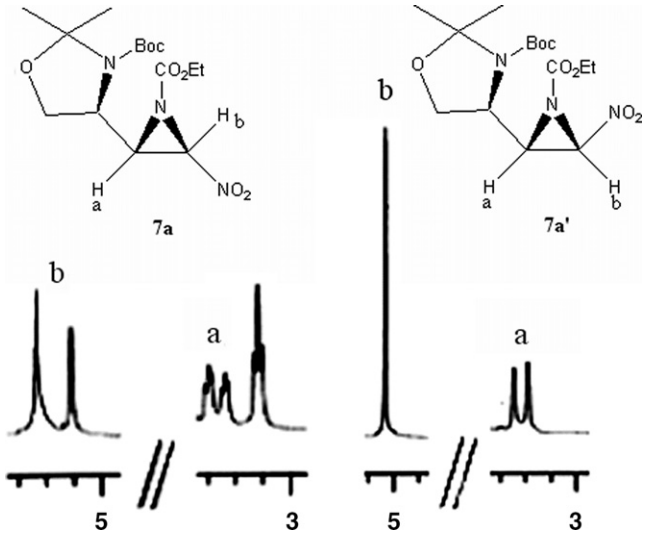


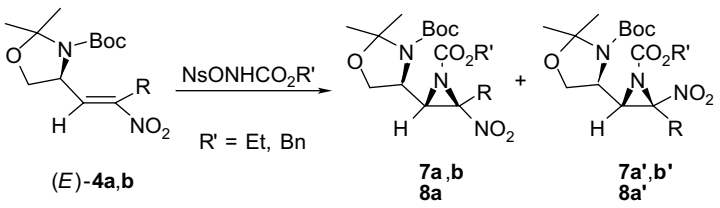
Figure 2.

Concerning the absolute configuration of the new chiral centres of these aziridines, X-ray analysis performed on **8a** showed that the nucleophilic attack of the aza-anion takes place on the *Si* face of chiral alkenes **4**. In Figure 3, the molecular structure of **8a** is shown. Ellipsoids are at 50% probability.

The choice between the two enantiomeric models (*RRR*) or (*SSS*) at the atoms C(3), C(7) and C(8), respectively, has been done on the basis of the known configuration of the C(3) atom.

Finally our interest was turned towards the useful chemical elaboration of optically active aziridines. In particular, we were interested to open selectively the dioxolane ring without affecting the aziridine.

Starting from the diastereomers **5a**,**a′**, a chemoselective hydrolysis of the dioxolane ring[11] with HCl led to the for-



Scheme 5.

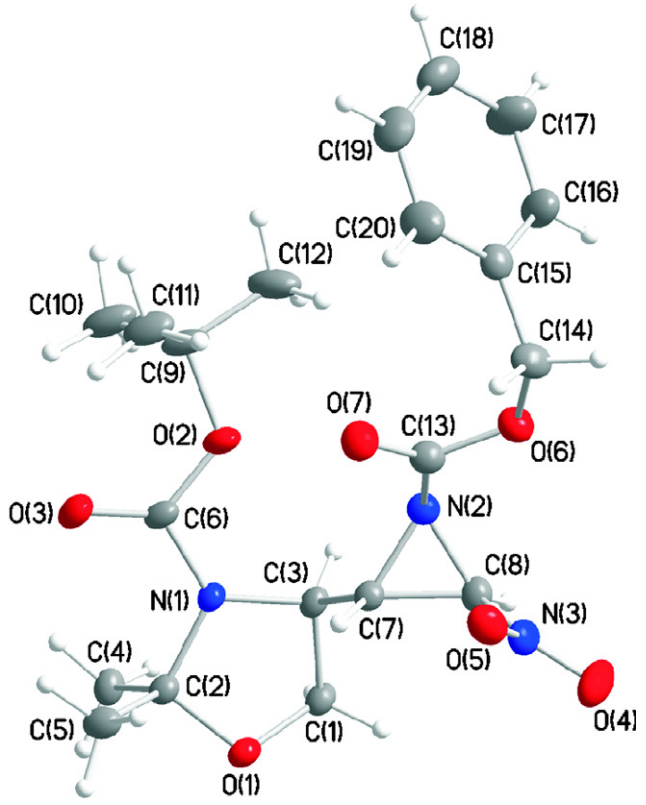
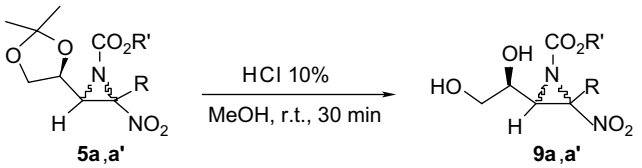


Figure 3.

mation of diastereomers **9a**,**a**′ in quantitative yield after 30 min (Scheme 6).



Scheme 6. Chemoselective hydrolysis of the dioxolane ring.

3. Conclusion

In conclusion, we have reported the synthesis of chiral functionalized aziridines, which can be considered useful building blocks, potential starting materials to obtain target molecules containing different sites of molecular growth.[12] Interestingly, the stereochemical outcome of aziridination reactions was strongly influenced by the chiral residue, giving stereoisomers, regardless of the reaction conditions.

4. Experimental

4.1. General methods

GC–MS analyses were performed with a HP G1800A gas chromatograph equipped with a capillary column (phenyl methyl silicone, 30 m × 0.25 mm). IR spectra were recorded on a PERKIN ELMER 1600 FT/IR spectrophotometer in $CHCl_3$ as the solvent, and reported in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz or at 200 and 50 MHz with a Varian XL-300 or Gemini 200 NMR spectrometer, respectively, and reported in δ units. $CDCl_3$ was used as the solvent and $CHCl_3$ as the internal standard. ESI MS analyses were performed using a Micromass Q-TOF Micro quadrupole-time of flight (TOF) mass spectrometer equipped with an ESI source and a syringe pump. The experiments were conducted in the positive ion mode. Optical rotations were determined with a JASCO DIP-370 polarimeter. HPLC analyses were performed with a VARIAN 9002 instrument using an analytical column (3.9 × 300 mm, flow rate 1.3 mL/min; detector: 254 nm) equipped with a VARIAN 9040 differential refractometer, or a VARIAN 9050 UV/VIS detector. Eluents were HPLC grade. Analytical thin-layer chromatography (TLC) was carried out on precoated silica gel plates. Silica gel 230–400 mesh was used for column chromatography. All solvents were dried following reported standard procedures.

4.1.1. Synthesis of optically active nitro alkenes. General procedure

4.1.1.1. Formation of nitro aldols. To a solution of enantiomerically pure aldehyde **1** or **2** (10 mmol, 1.0 equiv) in *i*-PrOH (20 mL) and benzene (2 mL) a suitable nitro alkane (50 mmol, 5.0 equiv) and KF (100 mg) were added. The mixture was stirred at room temperature for 24 h. Then CH_2Cl_2 (20 mL) was added and the solution was filtered through a pad of Celite. After evaporation of the solvents under reduced pressure the residue was dissolved in CH_2Cl_2, washed with saturated NaCl solution and dried with Na_2SO_4. Evaporation of the solvent under reduced pressure gave crude nitro aldols as diastereomeric mixtures, which were used in the dehydration step without further purification.

4.1.1.2. Dehydration of nitro aldols. Methylsulfonyl chloride (1.2 equiv) was added to a solution of crude nitro aldol (3.25 mmol, 1.0 equiv) in 20 mL of dry CH_2Cl_2 in one portion at 0 °C after 10 min followed by *i*-Pr_2NEt (2.5 equiv). The reaction mixture was allowed to warm to room temperature and washed with water, 2 M HCl and sat. NH_4Cl-solution. After drying with Na_2SO_4 the solvent was evaporated under reduced pressure and the remaining residue was purified by flash chromatography.

4.1.2. Synthesis of chiral nitro aziridines. General procedures. To an equimolar stirred solution of optically active nitro alkenes **3** and **4** and $NsONHCO_2R$ (R = Et,[13a] Bn[13b]), CaO or NaH (2 equiv) in CH_2Cl_2 or THF were added, respectively. After the reaction was complete (1–4 h, HPLC) the crude aziridines were filtered through plugs filled with silica gel using a 7/3 hexane/ethyl acetate eluent and products **5**–**8** were obtained as oils after solvent removal. The diastereomeric mixtures of nitro aziridines **7** and **8** were separated by HPLC using an 8/2 hexane/ethyl acetate mixture as the eluent (flow 1.3 mL/min).

4.1.3. Solvent-free synthesis of chiral nitro aziridines. General procedure. CaO (2 mmol), $NsONHCO_2Et$

(1 mmol) and optically active nitro alkenes (*E*)-**3a**, (*E*)-**3b** or (*E*)-**4b** (1 mmol) were ground together in a mortar for 30 min. The solid mixtures were dissolved with ethyl acetate and filtered through plugs filled with silica gel using a 7/3 hexane/ethyl acetate mixture. After evaporation of the solvents under reduced pressure, diastereomeric mixtures of corresponding nitro aziridines were obtained.

4.1.4. Ethyl (2*R*,3*S*)- and (2*S*,3*R*)-2-[(4′*S*)-2′,2′-dimethyl-1′,3′-dioxolan-4′-yl]-3-nitroaziridine-1-carboxylate 5a,a′. Pale yellow oil, 70–82%. IR: 1744, 1568 cm^{-1}. ^1H NMR: 1.28 (t, $J = 10$ Hz, 3H), 1.44 (s, 6H), 3.26 (d, $J = 1.5$ Hz, 1H), 3.32 (d, $J = 1.5$ Hz, 1H), 3.92 (m, 1H), 3.97 (m, 1H), 4.22 (m, 4H), 4.43 (m, 1H), 5.17 (d, $J = 1.5$ Hz, 1H), 5.2 (d, $J = 1.5$ Hz, 1H). ^{13}C NMR: 14.2, 24.8, 26.2, 26.8, 28.1, 46.0, 46.3, 62.9, 63.2, 71.4, 71.5, 110.8, 156.4, 157.9. HRMS (ES Q-TOF) calcd for $C_{10}H_{17}N_2O_6$ $(M+H)^+$: 261.1087; found: 261.1062.

4.1.5. Benzyl (2*R*,3*S*)- and (2*S*,3*R*)-2-[(4′*S*)-2′,2′-dimethyl-1′,3′-dioxolan-4′-yl]-3-nitroaziridine-1-carboxylate 6a,a′. Yellow oil, 75–85%. IR: 1743, 1565 cm^{-1}. ^1H NMR: 1.27 (s, 3H), 1.39 (s, 3H), 3.27 (dd, $J = 1.8$ Hz, 2.4 Hz, 1H), 3.35 (dd, $J = 1.2$ Hz, 1.5 Hz, 1H), 3.94 (m, 2H), 4.19 (m, 2H), 5.15 (m, 2H), 5.19 (s, 2H), 7.36 (m, 5H). ^{13}C NMR: 24.7, 24.8, 26.0, 46.5, 67.2, 69.3, 71.1, 110.8, 128.5, 128.9, 134.6, 156.4, 157.8. HRMS (ES Q-TOF) calcd for $C_{15}H_{17}N_2O_6$ $(M+H)^+$: 323.1243; found: 323.1207.

4.1.6. Ethyl (2*S*,3*R*)- and (2*R*,3*S*)-3-[(4′*S*)-2′,2′-dimethyl-1′,3′-dioxolan-4′-yl]-2-methyl-2-nitroaziridine-1-carboxylate 5b,b′. Yellow oil, 79%. IR: 1743, 1561 cm^{-1}. ^1H NMR: 1.33 (s, 3H), 1.42 (s, 3H), 1.97 (s, 3H), 1.98 (s, 3H), 2.78 (m, 1H), 3.32 (m, 1H), 4.18 (m, 5H). ^{13}C NMR: 14.2, 16.8, 25.1, 26.6, 49.2, 49.6, 63.5, 63.8, 67.7, 67.8, 110.7, 156.6, 157.2. HRMS (ES Q-TOF) calcd for $C_{11}H_{19}N_2O_6$ $(M+H)^+$: 275.1243; found: 275.1189.

4.1.7. *tert*-Butyl (4*S*)-4-[(2*S*,3*S*)-1-(ethoxycarbonyl)-3-nitroaziridin-2-yl]-2,2-dimethyl-1,3-oxazolidine-3-carboxylate 7a. Yellow oil, 32%. $[\alpha]_D = +2.2$ (*c* 1.0, $CHCl_3$). IR: 1743, 1696, 1566 cm^{-1}. ^1H NMR: 1.26 (t, $J = 7$ Hz, 3H), 1.46 (s, 9H), 1.50 (s, 6H), 3.24 (m, 1H), 3.52 (m, 1H), 4.11 (m, 4H), 5.22/5.47 (br s, 1H). ^{13}C NMR: 14.1, 22.9, 24.0, 28.2, 46.2, 57.3, 63.8, 81.8, 94.7, 153.6, 156.5. HRMS (ES Q-TOF) calcd for $C_{15}H_{26}N_3O_7$ $(M+H)^+$: 360.1771; found: 360.1749.

4.1.8. *tert*-Butyl (4*S*)-4-[(2*S*,3*R*)-1-(ethoxycarbonyl)-3-nitroaziridin-2-yl]-2,2-dimethyl-1,3-oxazolidine-3-carboxylate 7a′. Yellow oil, 49%. $[\alpha]_D = +1.9$ (*c* 1.0, $CHCl_3$). IR: 1743, 1696, 1566 cm^{-1}. ^1H NMR: 1.26 (t, $J = 7$ Hz, 3H), 1.47 (s, 9H), 1.56 (s, 6H), 3.38/3.44 (d, $J = 1.1$ Hz, 1H), 4.06 (m, 5H), 5.06 (d, $J = 1.1$ Hz, 1H). ^{13}C NMR: 14.0, 23.3, 26.5, 28.2, 44.9, 54.5, 63.5, 81.1, 94.6, 151.0, 156.2. HRMS (ES Q-TOF) calcd for $C_{15}H_{26}N_3O_7$ $(M+H)^+$: 360.1771; found: 360.1746.

4.1.9. *tert*-Butyl (4*S*)-4-[(2′*S*,3′*S*)-1′-(ethoxycarbonyl)-3′-methyl-3′-nitroaziridin-2′-yl]-2,2-dimethyl-1,3-oxazolidine-3-carboxylate 7b. Yellow oil, 55%. $[\alpha]_D = +1.9$ (*c* 1.0, $CHCl_3$). IR: 1743, 1698, 1561 cm^{-1}. ^1H NMR: 1.25 (s, 6H), 1.45 (s, 3H), 1.48 (s, 9H) 1.93/2.03 (s, 3H), 3.44 (m, 1H), 4.12 (m, 4H), 5.29 (s, 1H). ^{13}C NMR: 14.4, 23.1, 25.1, 26.5, 28.2, 44.2, 54.5, 63.2, 81.8, 94.5, 151.4, 156.0. HRMS (ES Q-TOF) calcd for $C_{16}H_{28}N_3O_7$ $(M+H)^+$: 374.1927; found: 374.1891.

4.1.10. *tert*-Butyl (4*S*)-4-[(2′*S*,3′*R*)-1′-(ethoxycarbonyl)-3′-methyl-3′-nitroaziridin-2′-yl]-2,2-dimethyl-1,3-oxazolidine-3-carboxylate 7b′. Yellow oil, 23%. $[\alpha]_D = +2.15$ (*c* 1.0, $CHCl_3$). IR: 1743, 1698, 1561 cm^{-1}. ^1H NMR: 1.12 (s, 6H), 1.35 (s, 9H), 1.46 (s, 3H) 2.01 (s, 3H), 3.41 (m, 1H), 4.05 (m, 5H). ^{13}C NMR: 14.4, 23.0, 25.4, 26.8, 29.2, 44.3, 54.6, 63.2, 81.8, 97.5, 151.4, 156.0. HRMS (ES Q-TOF) calcd for $C_{16}H_{28}N_3O_7$ $(M+H)^+$: 374.1927; found: 374.1894.

4.1.11. *tert*-Butyl (4*S*)-4-{(2′*S*,3′*S*)-1′-[(phenylmethoxy)carbonyl]-3′-nitroaziridin-2′-yl}-2,2-dimethyl-1,3-oxazolidine-3-carboxylate 8a. White solid, 47%. mp 89–91 °C. $[\alpha]_D = +2.7$ (*c* 1.0, $CHCl_3$). IR: 1743, 1702, 1566 cm^{-1}. ^1H NMR: 1.47 (s, 3H), 1.49 (s, 3H), 3.27 (dd, $J = 0.7$ Hz, 7.8 Hz, 1H), 3.45/3.58 (m, 1H), 4.01/4.13 (m, 2H), 5.16 (m, 1H), 5.21/5.24 (br, 1H), 7.34 (m, 5H). ^{13}C NMR: 22.7, 24.0, 28.2, 46.0/46.5, 56.7/57.2, 69.4/69.8, 81.3, 95.1, 128.5, 128.6, 128.7, 151.2, 152.4, 156.4. HRMS (ES Q-TOF) calcd for $C_{20}H_{28}N_3O_7$ $(M+H)^+$: 422.1927; found: 422.1866.

4.1.12. X-ray crystallographic study of 8a. Colourless thin needles of **8a** were grown by slow evaporation of a saturated hexane solution. In spite of the relatively good crystal quality, their low diffracting power and the too small dimensions prevented a diffraction study on a home diffractometer. X-ray crystallographic analysis was then performed using synchrotron radiation data, collected at ELETTRA (XRD-1 beam line), Trieste (Italy), $\lambda = 0.700087$ Å. A marCCD detector (marUSA Inc., USA) and focusing optics were employed for the measurements. Ninety images were collected at 100 K and a 4° oscillation range was used for all images. The degree of linear polarization was assumed to be 0.95 and the mosaic spread of the crystal was estimated to be 0.54°. Raw data were indexed, integrated, scaled, and reduced using the HKL[14] package. The specimen used (15 μm × 30 μm × 280 μm) belongs to the orthorhombic system with unit cell: $a = 17.937(1)$, $b = 5.739(1)$, $c = 20.731(2)$, space group $P2_12_12_1$, $Z = 4$, $\mu = 0.120$ mm^{-1} and $D_c = 1.312$ g cm^{-3}. The intensity data were merged to give 7990 unique reflections, merging $R = 0.0243$, of which 6816 with $I \geqslant 2\sigma(I)$. The structure was solved by SHELXS-97[15] and refined by full-matrix least-squares procedures. Hydrogen atoms were located from a difference Fourier map. In the final refinement cycle anisotropic thermal parameters were used for all of the nonhydrogen atoms, while hydrogen ones were refined isotropically using a riding model. The final residuals were $R_1 = 0.0507$, $wR_2 = 0.1218$ for the 6816 observed reflections and 0.0634, 0.1298 for all data and 277 parameters. Goof = 1.087, maximum $\Delta\rho = 0.452$ e $Å^{-3}$. All calculations were performed on a microcomputer using SHELXL-97 and WINGX programs.[15,16] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge

Crystallographic Data Centre as supplementary publication no. CCDC-666872. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk].

4.1.13. *tert*-Butyl (4*S*)-4-{(2′*S*,3′*R*)-1′-[(phenylmethoxy)carbonyl]-3′-nitroaziridin-2′-yl}-2,2-dimethyl-1,3-oxazolidine-3-carboxylate 8a′. White solid, 32%. mp 95–97 °C. $[\alpha]_D = +2.0$ (*c* 1.0, $CHCl_3$). IR: 1743, 1702, 1566 cm^{-1}. ^1H NMR: 1.45 (s, 3H), 1.47 (s, 3H), 3.28 (dd, $J = 0.7$ Hz, 7.8 Hz, 1H), 3.82 (m, 2H), 5.08 (s, 2H), 5.16 (m, 1H), 5.21/5.24 (br, 1H), 7.34 (m, 5H). ^{13}C NMR: 14.0, 22.5, 28.2, 54.4, 67.8/69.3, 128.4, 128.5, 128.6, 156.1. HRMS (ES Q-TOF) calcd for $C_{20}H_{28}N_3O_7$ $(M+H)^+$: 422.1927; found: 422.1860.

4.1.14. Ethyl (2*R*,3*S*) and (2*S*,3*R*)-2-[(1′*S*)-1′,2′-dihydroxyethyl]-3-nitroaziridine-1-carboxylate 9a,a′. Pale yellow oil. IR: 3630, 1744, 1568 cm^{-1}. ^1H NMR: 1.25 (s, 3 H), 1.60 (s, 1H), 3.66 (d, $J = 1.5$ Hz, 1H), 3.75 (d, $J = 1.5$ Hz, 1H), 4.14 (m, 6H), 5.35 (d, $J = 1.5$ Hz, 1H), 5.14 (d, $J = 1.5$ Hz, 1H). ^{13}C NMR: 46.4, 46.8, 63.0, 63.2, 71.4, 71.8, 111.4, 156.7, 157.1. HRMS (ES Q-TOF) calcd for $C_7H_{13}N_2O_6$ $(M+H)^+$: 221.0774; found: 221.0790.

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