Regio- and Stereoselective Lithiation of Terminal Oxazolinylaziridines: the Aziridine *N*-Substituent and the Oxazolinyl Group Effect

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General. Tetrahydrofuran (THF) and diethylether were freshly distilled under a nitrogen over sodium/benzophenone ketyl. Toluene and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled over finely powdered CaH₂. For the ¹H and ¹³C NMR spectra (¹H NMR 300, 400, 500, 600 MHz, ¹³C NMR 75.4, 100, 125, 150 MHz), CDCl₃, CD₃OD, THF-*d*₈ were used as the solvents. MS-ESI analyses were performed on LC/MSD trap system VL. Melting points were uncorrected. Analytical thin layer chromatography (TLC) was carried out on precoated 0.25 mm thick plates of Kieselgel 60 F254, visualization was accomplished by UV light (254 nm) or by spraying a solution of 5 % (w/v) ammonium molybdate and 0.2 % (w/v) cerium(III) sulfate in 100 ml 17.6 % (w/v) aq. sulphuric acid and heating to 200 °C for some time until blue spots appear. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe-septum cap technique.

Experimental Section

Preparation of oxazolinylaziridines 3a-c.

The investigated aziridines were prepared starting from the corresponding aziridinecarboxylate **1a-c** which in turn were transformed into amides **2a-c** and then converted into the corresponding oxazolinylaziridines **3a-c** (Scheme1) by modification of reported procedures.¹

i: RNH₂ (PhCH₂NH₂ or PhC(CH₃)₂NH₂), EtOH, RT. ii: 2-methyl-2-aminopropanol, n-BuLi, LaCl₃, toluene. iii: Et₂NSF₃, CH₂Cl₂. iv: Ph₃CBr, NaH, THF.

¹ a) Trost, B. M.; Fandrick, D. R. *Org. Lett.* **2005**, 7, 823–826 b) Zhou, P.; Blubaum, J. E.; Burns, C. T.; Natale, N. R. *Tetrahedron Lett.* **1997**, 38, 7019-7022. c) Phillips, A. J.; Uto, Y.; Wipf, P.; Reno, M. J.; Williams, D. R. *Org. Lett.* **2000**, 8, 1165-1168. d) Ahman, J.; Somfai, P. *Synth. Comm.* **1994**, 1121-1127.

Preparation of aziridines **1a**.^{1d}

To a suspension of commercially available methyl aziridine-2-carboxylate (1 mmol) in dry THF (25 mL), *ans* NaH (1.1 mmol) was added a solution of trityl bromide (Ph₃CBr) (1 mmol) in dry THF (10 mL) and the resulting mixture stirred at room temperature for 24 h. After this time the mixture was poured in cold water and extracted with Et₂O (3 × 10 mL). The combined organic layers were dried (Na₂SO₄) and the solvent evaporated in *vacuo*. The crude was dissolved in hexane and the white solid of unreacted Ph₃CBr filtered off. The solvent was removed to furnish a crude containing the aziridine **2a** in 40 % yield that was used without further purification.

Preparation of aziridines **1b,c**.^{1a}

The suitable amine (PhC(CH₃)₂NH₂ 10 mmol for **1b** or BnNH₂, 10 mmol for **1c**) followed by Et₃N (20 mmol) were added to a solution of ethyl 2,3-dibromopropanoate (20 mmol) in anhydrous ethanol (150 mL) at 0°C under nitrogen. The reaction was allowed to warm to room temperature and stirred at 50°C in a sealed flask for 3 h. The resulting yellow solution was concentrated in *vacuo* to an oily solid. The oily solid was suspended in ether (150 mL) and vigorously stirred for 1 h. The solids were removed by filtration and rinsed thoroughly with ether. The filtrate was concentrated in *vacuo* to afford the intended aziridine (**1b** or **1c**) as a yellow oil (> 93%). This material could be used in the next step without further purification. Aziridine **1c** should be used soon after the preparation because of the limited stability even if stored at low temperature.

(±)-Ethyl-1-(2-phenylpropan-2-yl)aziridine-2-carboxylate 1b (93%), yellow oil. ¹H NMR (CDCl₃, 400 MHz) δ: 1.19 (t, *J* = 7.0 Hz, 3 H), 1.33 (s, 3 H), 1.39 (s, 3 H), 1.64 (dd, *J* = 6.2, 1.5 Hz, 1 H), 1.98 (dd, *J* = 3.0, 1.5 Hz, 1 H), 2.03 (dd, *J* = 6.2, 3.0 Hz, 1 H), 4.08-4.16 (m, 2 H), 7.17-7.28 (m, 3 H), 7.37 (d, *J* = 8.0 Hz, 2 H). ¹³C NMR (CDCl₃, 150 MHz) δ: 14.1, 25.3, 27.5, 28.2, 31.4, 58.8, 60.8, 126.4, 126.8, 127.9, 143.8, 171.4. ESI-MS *m/z* (rel. int): 256 [M+Na]⁺ (100). FT-IR (film) cm⁻¹: 2977, 1741, 1494, 1445, 1383, 1281, 1237, 1188, 1031, 765.

(±)-Ethyl-1-benzylaziridine-2-carboxylate 1c: (93%), yellow oil. ¹H NMR (CDCl₃, 500 MHz) δ: 1.18 (t, *J* = 7.1 Hz, 3 H), 1.66 (dd, *J* = 6.3, 1.2 Hz, 1 H), 2.11 (dd, *J* = 6.3, 3.2 Hz, 1 H), 2.18 (dd, *J* = 3.2, 1.2 Hz, 1 H), 3.46-3.48 (m, 2 H), 4.05-4.16 (m, 2 H), 7.17-7.28 (m, 5 H). ¹³C NMR (CDCl₃, 125 MHz) δ: 14.2, 34.5, 37.5, 61.1, 63.8, 127.3, 128.0, 128.4, 137.8, 170.7. ESI-MS *m/z* (rel. int): 228 [M+Na]⁺ (100). FT-IR (film) cm⁻¹: 3027, 2978, 1725, 1494, 1453, 1403, 1187, 1109, 735.

General procedure for the preparation of aziridines **2a-c**.^{1b}

To a perfectly dry flask charged with anhydrous LaCl_3 (0.1 mmol) were added 20 mL of dry toluene and 2-methyl-2-amino-1-propanol (2.5 mmol), then $n\text{-BuLi}$ (2.2 mmol of a 1.4 M cyclohexane solution) was added to this suspension at 0 °C and the reaction stirred at this temperature for 15 minutes. After this time the flask was warmed up to 100 °C for **2a**, 30 °C for **2b** and to room temperature for **2c**. Aziridincarboxylate (**1a-c**) was added and the resulting mixture stirred at the indicated temperature for 12 h in the case of **2a**, 2 h in the case of **2b** and 30 min. in the case of **2c**. The suspension was filtered, concentrated under reduced pressure and then poured in water and extracted with chloroform (3×15 mL). The combined organic layers were dried (Na_2SO_4) and the solvent evaporated in *vacuo*. The crude containing **2a** (95%) or **2b** (85 %) can be used in the next step without further purification; in the case of **2c** (70 %) the product was isolated by flash chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ 95/5).

(±)-N-(1-Hydroxy-2-methylpropan-2-yl)-1-(2-phenylpropan-2-yl)aziridine-2-carboxamide 2b: (85%), white oil. ^1H NMR (CDCl_3 , 400 MHz) δ : 1.22 (s, 3 H), 1.24 (s, 3 H), 1.39 (s, 3 H), 1.39 (s, 3 H), 1.73 (dd, $J = 2.7, 0.8$ Hz, 1 H), 1.79 (dd, $J = 6.8, 0.8$ Hz, 1 H), 2.14 (dd, $J = 6.8, 2.7$ Hz, 1 H), 3.52 -3.58 (m, 2 H), 5.10 (bs, 1 H), 6.82 (bs, 1 H), 7.17 -7.42 (m, 5 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 24.7, 25.0, 26.1, 26.1, 29.6, 33.3, 55.6, 55.1, 70.7, 126.1, 127.1, 128.2, 144.1, 171.8. ESI-MS m/z (rel. int): 299 $[\text{M}+\text{Na}]^+$ (100). FT-IR (film) cm^{-1} : 3343, 2975, 1654, 1529, 1496, 1448, 1262, 1063, 765.

(±)-1-Benzyl-N-(1-hydroxy-2-methylpropan-2-yl)aziridine-2-carboxamide 2c: (70%), white oil. ^1H NMR (CDCl_3 , 500 MHz) δ : 1.16 (s, 3 H), 1.17 (s, 3 H), 1.73 (d, $J = 7.1$ Hz, 1 H), 1.89 (d, $J = 3.2$ Hz, 1 H), 2.1 (dd, $J = 7.1$ Hz, 3.2 Hz, 1 H), 3.40-3.56 (2 $\times$ d, AB system, $J = 13.5$ Hz, 2 H), 3.45-3.51 (m, 2 H), 4.93 (bs, 1 H), 6.57 (bs, 1 H), 7.21-7.33 (m, 5 H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 24.4, 24.7, 35.3, 39.1, 55.5, 62.6, 70.3, 127.4, 127.8, 128.4, 137.7, 171.1. ESI-MS m/z (rel. int): 271 $[\text{M}+\text{Na}]^+$ (100). FT-IR (film) cm^{-1} : 3342, 2974, 1658, 1531, 1455, 1360, 1278, 1064, 732.

General procedure for the preparation of oxazolinylaziridines **3a-c**.^{1c}

To a cold solution in dry CH₂Cl₂ (10 mL) of the β -hydroxyamide (-78 °C for **3a** and -98 °C for **3b,c**) (1 mmol), diethylaminosulfurtrifluoride (DAST) (1.1 mmol) is added dropwise and the mixture stirred at the indicated temperature for 3h. After this time anhydrous K₂CO₃ (1.5 mmol) was added in one portion and the resulting mixture warmed to room temperature, poured in into saturated aqueous NaHCO₃ and the biphasic mixture extracted with CH₂Cl₂ (3 $\times$ 15 mL). The combined organic layers were dried (Na₂SO₄) and the solvent evaporated in *vacuo*. The crude containing **3a** (80 %) as a white solid can be used without further purification; by kugelrohr distillation under vacuum (10⁻⁵ torr.) was possible to isolate **3b** (35 %) and **3c** (40 %) as clear oil.

($\pm$)-4,4-Dimethyl-2-(1-tritylaziridin-2-yl)-4,5-dihydrooxazole **3a:** (80%), white solid, mp: 168-170 °C. ¹H NMR (CDCl₃, 500 MHz) δ : 1.30, (s, 3 H), 1.33 (s, 3 H), 1.40 (dd, J = 6.1 Hz, 3.0 Hz, 1 H), 1.98 (dd, J = 6.1, 1.0 Hz, 1 H), 2.27 (dd, J = 3.0, 1.0 Hz, 1 H), 3.97-4.10 (2 $\times$ d, AB system, J = 8.5 Hz, 2 H), 7.19-7.28 (m, 9 H), 7.48-7.50 (m, 6 H). ¹³C NMR (THF-*d*₈, 100 MHz) δ : 27.5, 28.4, 28.7, 29.1, 68.1, 75.2, 79.6, 127.5, 127.6, 128.1, 128.3, 130.2, 130.3, 144.9, 164.0. ESI-MS m/z (rel. int.): 405 [M+Na]⁺ (100). FT-IR (KBr) cm⁻¹: 2958, 1664, 1489, 1449, 1301, 1005, 708.

(S)-4,4-dimethyl-2-(1-tritylaziridin-2-yl)-4,5-dihydrooxazole (S)-3a**:** er 99:1; [α]_D²⁰ (c = 0.8, CHCl₃) = - 83.7.

($\pm$)-4,4-Dimethyl-2-(1-cumylaziridin-2-yl)-4,5-dihydrooxazole **3b:** (35%), colourless oil. ¹H NMR (CDCl₃, 600 MHz) δ : 1.26 (s, 3 H), 1.29 (s, 3 H), 1.43 (s, 3 H), 1.49 (s, 3 H), 1.66 (d, J = 6.4 Hz, 1 H), 2.04 (d, J = 3.1 Hz, 1 H), 2.22 (dd, J = 6.4, 2.1 Hz, 1 H), 3.90-3.99 (2 $\times$ d, AB system, J = 7.9 Hz, 2 H), 7.23-7.44 (m, 5 H). ¹³C NMR (CDCl₃, 150 MHz) δ : 25.7, 27.3, 27.4, 28.2, 28.2, 28.3, 58.9, 67.0, 79.2, 126.6, 126.8, 127.9, 143.3, 164.1. ESI-MS m/z (rel. int.): 259 [M+H]⁺ (100). FT-IR (film) cm⁻¹: 2894, 1660, 1518, 1495, 1462, 1384, 1363, 1301, 1229, 1102, 1031, 765.

($\pm$)-2-(1-Benzylaziridin-2-yl)-4,4-dimethyl-4,5-dihydrooxazole **3c:** (40%), waxy solid, mp: 40 – 42 °C. ¹H NMR (CDCl₃, 500 MHz) δ : 1.26 (s, 3 H), 1.28 (s, 3 H), 1.70 (d, J = 6.3 Hz, 1 H), 2.24 (d, J = 3.1 Hz, 1 H), 2.31 (dd, J = 6.3, 3.1 Hz, 2 H), 3.35-3.77 (2 $\times$ d, AB system, J = 13.5 Hz, 2 H), 3.91-3.98 (2 $\times$ d, AB system, J = 8.1 Hz, 2 H), 7.24-7.36 (m, 5 H). ¹³C NMR (CDCl₃, 125 MHz) δ : 28.1, 28.1, 33.3, 34.1, 63.9, 67.0, 79.1, 127.0, 127.9, 128.1, 137.7, 163.2. ESI-MS m/z (rel. int.): 231 [M+H]⁺ (100). FT-IR (film) cm⁻¹: 2969, 1665, 1454, 1351, 1301, 1252, 1199, 1004, 736.

General procedure for the lithiation-trapping sequence of aziridines 3a:

To a solution of the aziridines **3a** (1 mmol) and TMEDA (2.0 mmol) in 10 mL of dry THF, at -70°C and under N_2 , *s*-BuLi (2.0 mmol of a 1.4 M cyclohexane solution) was added dropwise. The resulting reddish mixture was stirred for 2 h at this temperature before quenching with the electrophile (neat if liquid or diluted in 2 mL of THF if solid). The reaction mixture was warmed up to room temperature and a solution of sat. aq. NH_4Cl (3 mL) was added, the mixture poured in 20 mL of water and extracted with Et_2O (3×10 mL). The combined organic layers were dried (Na_2SO_4) and the solvent evaporated in *vacuo*. The crude was purified by flash chromatography on silica gel (AcOEt/Petroleum Ether) to furnish aziridines **5a-j** and **6a-g**.

(2*R,3*R**)-4,4-Dimethyl-2-(1-trityl-3-deuterioaziridin-2-yl)-4,5-dihydrooxazole 5a:** 90%, 87 %D, white solid, mp: $168 - 170^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 500 MHz) δ : 1.30, (s, 3 H), 1.33 (s, 3 H), 1.40 (d, $J = 6.1$ Hz, 1 H), 1.98 (d, $J = 6.1$ Hz, 1 H), 2.27 (dd, $J = 3.0$, 1 Hz, 1 H), 3.97-4.10 ($2 \times$ d, AB system, $J = 8.5$ Hz, 2 H), 7.19-7.28 (m, 9 H), 7.48-7.50 (m, 6 H). ^{13}C NMR ($\text{THF}-d_8$, 100 MHz) δ : 27.5, 28.4, 28.7, 29.1, 68.1, 75.2, 79.6, 127.5, 127.6, 128.1, 128.3, 130.2, 130.3, 144.9, 164.0. ESI-MS m/z (rel. int): 406 $[\text{M}+\text{Na}]^+$ (100). FT-IR (KBr) cm^{-1} : 2958, 1664, 1489, 1449, 1301, 1005, 708.

(2*R,3*S**)-4,4-Dimethyl-2-(1-trityl-3-trimethylsililaziridin-2-yl)-4,5-dihydrooxazole 5b:** 70%, colourless oil. ^1H NMR (CDCl_3 , 500 MHz) δ : 0.12 (s, 9 H), 0.64 (d, $J = 7.1$, 1 H), 1.30 (s, 3 H), 1.33 (s, 3 H), 1.96 (d, $J = 7.1$, 1 H), 3.93-4.08 ($2 \times$ d, AB system, $J = 8.1$ Hz, 2 H), 7.19-7.27 (m, 9 H), 7.54-7.56 (m, 6 H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : -1.2, 28.2, 28.4, 29.2, 31.9, 67.1, 75.7, 78.9, 126.6, 127.3, 129.6, 143.6, 164.7. ESI-MS m/z (rel. int): 477 $[\text{M}+\text{Na}]^+$ (100). FT-IR (film) cm^{-1} : 3060, 2964, 1661, 1489, 1448, 1248, 1189, 908.

(2*R*,3*S*)-4,4-Dimethyl-2-(3-trimethylsilil-1-tritylaziridin-2-yl)-4,5-dihydrooxazole: (presumed er 99:1), $[\alpha]_{\text{D}}^{20}$ ($c = 1.5$, CHCl_3) = -69.4.

(2*R,3*R**)-4,4-Dimethyl-2-(3-methyl-1-tritylaziridin-2-yl)-4,5-dihydrooxazole 5c:** 75%, white oil. ¹H NMR (CDCl₃, 500 MHz) δ : 1.33, (s, 6 H), 1.40 (d, *J* = 5.5 Hz, 3 H), 1.55-1.60 (m, 1 H), 1.95 (d, *J* = 6.3 Hz, 1 H), 3.98-4.04 (2 × d, AB system, *J* = 7.9 Hz, 2 H), 7.19-7.27 (m, 9 H), 7.53 - 7.55 (m, 6 H). ¹³C NMR (CDCl₃, 125 MHz) δ: 13.3, 28.4, 32.1, 34.3, 62.7, 75.1, 79.0, 126.7, 127.4, 129.5, 143.9, 163.6. ESI-MS *m/z* (rel. int): 419 [M+Na]⁺ (100). FT-IR (film) cm⁻¹: 2967, 1670, 1654, 1489, 1447, 1163, 1119, 708.

(2*S*,3*S*)-4,4-Dimethyl-2-(3-methyl-1-tritylaziridin-2-yl)-4,5-dihydrooxazole: er: 99:1; [α]²⁰_D (c=1, CHCl₃) = -102.7.

(2*R,3*R**)-4,4-Dimethyl-2-(3-benzyl-1-tritylaziridin-2-yl)-4,5-dihydrooxazole 5d:** 55%, yellow oil. ¹H NMR (CDCl₃, 500 MHz) δ: 1.29 (s, 3 H), 1.33 (s, 3 H), 1.79-1.83 (m, 1 H), 2.05 (d, *J* = 5.9 Hz, 1 H), 3.23-3.33 (m, 2 H), 3.98-4.02 (2 × d, AB system, *J* = 8.3 Hz, 2 H), 7.07-7.28 (m, 14 H), 7.55-7.56 (m, 6 H). ¹³C NMR (CDCl₃, 125 MHz) δ: 28.3, 28.4, 32.1, 34.2, 39.9, 67.3, 75.2, 79.1, 126.1, 126.8, 127.5, 128.3, 128.5, 129.5, 139.0, 143.8, 163.5. ESI/MS *m/z* (rel. int): 495 [M+Na]⁺ (100). FT-IR (film) cm⁻¹: 3063, 2965, 1668, 1495, 1448, 1362, 1226, 1155, 997, 708.

(2*S*,3*S*)-4,4-Dimethyl-2-(3-benzyl-1-tritylaziridin-2-yl)-4,5-dihydrooxazole er: 99:1; [α]²⁰_D (c = 0.5, CHCl₃) = +3.9.

(2*R,3*S**)-4,4-Dimethyl-2-(3-tributylstannyl-1-tritylaziridin-2-yl)-4,5-dihydrooxazole 5e:** 75%, colourless oil. ¹H NMR (CDCl₃, 500 MHz) δ: 0.84-0.87 (m, 7 H), 0.92-0.99 (m, 7 H), 1.13 (d, *J* = 6.7 Hz, 1 H), 1.24-1.29 (m, 9H), 1.32 (s, 3H), 1.40-1.46 (m, 6H), 1.62-1.69 (m, 1H), 1.93 (d, *J* = 6.7 Hz, 1 H), 3.85-4.08 (2 × d, AB system *J* = 7.9 Hz, 2 H), 7.16-7.26 (m, 9 H), 7.47-7.48 (m, 6 H). ¹³C NMR (CDCl₃, 150 MHz) δ: 10.5, 13.7, 27.4, 28.2, 28.7, 29.2, 31.3, 67.2, 76.0, 79.2, 126.7, 127.4, 129.5, 143.8, 165.5. ESI/MS *m/z* (rel. int): 673 [M+H]⁺ (100). FT-IR (film) cm⁻¹: 3059, 2957, 2924, 1741, 1668, 1596, 1490, 1448, 1375, 1247, 1191, 1034, 970, 762.

(2*R*,3*S*)-4,4-Dimethyl-2-(3-tributylstannyl-1-tritylaziridin-2-yl)-4,5-dihydrooxazole er: 99:1; [α]²⁰_D (c = 0.66, CHCl₃) = +19.8.

(2*R,3*S**)-4,4-Dimethyl-2-(3-dimethylallylsilyl-1-tritylaziridin-2-yl)-4,5-dihydrooxazole 5f:**

70%, white solid, mp: 178-180 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 0.09 (s, 3 H), 0.21 (s, 3 H), 0.71 (d, *J* = 7.0, 1 H), 1.30 (s, 3 H), 1.33 (s, 3 H), 1.56-1.60 (m, 2 H), 1.96 (d, *J* = 7.0 Hz, 1 H), 3.94-4.09 (2 × d, AB system, *J* = 8.0 Hz, 2 H), 4.72-4.78 (m, 2 H), 5.63-5.69 (m, 1 H), 7.18-7.28 (m, 9 H), 7.53-7.55 (m, 6 H). ¹³C NMR (CDCl₃, 100 MHz) δ: -3.7, -3.2, 23.7, 27.9, 28.2, 28.5, 32.0, 67.2, 75.8, 78.9, 113.1, 126.7, 127.3, 129.6, 134.5, 143.4, 164.6. ESI/MS *m/z* (rel. int): 481 [M+H]⁺ (100). FT-IR (KBr) cm⁻¹: 3059, 2966, 2926, 1740, 1658, 1630, 1490, 1448, 1364, 1248, 1155, 1047, 945, 896, 836.

(2*R*,3*S*)-4,4-Dimethyl-2-(3-dimethylallylsilyl-1-tritylaziridin-2-yl)-4,5-dihydrooxazole: er: 99:1; [α]_D²⁰ (c = 0.5, CHCl₃) = -36.6.

(2*R,3*R**)-4,4-Dimethyl-2-(3-ethyl-1-tritylaziridin-2-yl)-4,5-dihydrooxazole 5g: 60%,**

colourless oil. ¹H NMR (CDCl₃, 600 MHz) δ: 0.85 (t, *J* = 7.7 Hz, 3 H), 1.35 (s, 6 H), 1.45-1.47 (m, 1 H), 1.77-1.85 (m, 1 H), 1.98 (d, *J* = 6.6 Hz, 1 H), 2.00-2.05 (m, 1 H), 4.01-4.05 (2 × d, AB system, *J* = 8.2 Hz, 2 H), 7.21-7.30 (m, 9 H), 7.57-7.58 (m, 6 H). ¹³C NMR (CDCl₃, 150 MHz) δ: 11.4, 21.7, 28.3, 28.3, 31.7, 40.9, 67.2, 75.0, 79.1, 126.7, 127.4, 129.5, 144.0, 163.7. ESI/MS *m/z* (rel. int): 433 [M+Na]⁺ (100). FT-IR (film) cm⁻¹: 3057, 3033, 2964, 1669, 1655, 1490, 1448, 1364, 1225, 1157, 1001, 708.

(2*S*,3*S*)-4,4-Dimethyl-2-(3-ethyl-1-tritylaziridin-2-yl)-4,5-dihydrooxazole (presumed er: 99:1); [α]_D²⁰ (c = 0.6, CHCl₃) = -66.8.

(2*R,3*R**)-2-(3-Allyl-1-tritylaziridin-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 5h: 66%, colourless**

oil. ¹H NMR (CDCl₃, 500 MHz) δ: 1.32, (s, 3 H), 1.33, (s, 3 H), 1.55-1.60 (m, 1 H), 2.0 (d, *J* = 6.1 Hz, 1 H), 2.55-2.61 (m, 1 H), 2.72-2.77 (m, 1 H), (3.98-4.03, 2 × d, AB system, *J* = 7.9 Hz, 2 H), 4.92 (dd, *J* = 10.4, 1.8 Hz 1 H) 4.97-5.01 (m, 1 H), 5.63-5.71 (m, 1 H), 7.19-7.27 (m, 9 H), 7.53 - 7.54 (m, 6 H). ¹³C NMR (CDCl₃, 125 MHz) δ: 28.3, 31.7, 32.8, 38.4, 65.2, 75.0, 79.1, 116.2, 126.8, 127.5, 129.5, 135.0, 143.8, 163.5. ESI-MS *m/z* (rel. int): 445 [M+Na]⁺ (100). FT-IR (film) cm⁻¹: 2967, 1670, 1654, 1489, 1447, 1163, 1119, 708.

(2*S*,3*S*)-2-(3-Allyl-1-tritylaziridin-2-yl)-4,4-dimethyl-4,5-dihydrooxazole (presumed er: 99:1); [α]_D²⁰ (c = 1, CHCl₃) = -29.4.

(2*R,3*S**)-2-(3-Benzoyl-1-tritylaziridin-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 5i:** 70%, white solid, mp: 112 – 114 °C. ¹H NMR (CDCl₃, 600 MHz) δ: 0.9 (s, 3 H), 0.17 (s, 3 H), 2.64-2.84 (2 × d, AB system, *J* = 6.6 Hz, 2 H), 3.54 -3.93 (2 × d, AB system, *J* = 8.2 Hz, 2 H), 7.24-7.33 (m, 9 H), 7.38 (t, *J* = 7.7 Hz, 2 H), 7.51 (t, *J* = 7.1 Hz 1 H), 7.71-7.72 (m, 6 H), 7.82-7.83 (d, *J* = 7.1 Hz, 2 H). ¹³C NMR (CDCl₃, 125 MHz) δ: 27.9, 28.0, 34.8, 42.3, 67.1, 75.1, 79.5, 127.1, 127.7, 128.1, 128.5, 129.5, 133.2, 136.1, 143.1, 161.7, 192.4. ESI-MS *m/z* (rel. int): 509 [M+Na]⁺ (100). FT-IR (KBr) cm⁻¹: 2966, 1696, 1661, 1448, 1224, 1001.

(2*R,3*S**)-4,4-Dimethyl-2-(3-phenylthio-1-tritylaziridin-2-yl)-4,5-dihydrooxazole 5j:** 50%, colourless oil. ¹H NMR (CDCl₃, 500 MHz) δ: 1.23 (s, 3H), 1.28 (s, 3H), 2.39 (d, *J* = 5.5 Hz, 1 H); 2.90 (d, *J* = 5.5 Hz, 1 H); 4.01-4.09 (2 × d, AB system *J* = 7.9, 2 H); 7.10-7.28 (m, 14 H); 7.52-7.54 (m, 6 H). ¹³C NMR (CDCl₃, 125 MHz) δ: 28.2, 29.6, 34.0, 46.4, 67.4, 76.0, 79.4, 126.5, 127.0, 127.7, 128.7, 129.3, 130.2, 134.9, 142.8, 161.0. ESI/MS *m/z* (rel. int): 491 [M+H]⁺ (100). FT-IR (film) cm⁻¹: 3058, 2964, 2926, 1967, 1737, 1658, 1584, 1490, 1365, 1305, 1190, 1013, 973, 746, 631.

(2*R*,3*S*)-4,4-Dimethyl-2-(3-phenylthio-1-tritylaziridin-2-yl)-4,5-dihydrooxazole: er: 99:1; [α]_D²⁰ (c = 0.4, CHCl₃) = + 90.

(2*R,3*S**)-3-[2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]pentan-3-ol 6a:** 60%, white solid, mp: 150 – 153 °C. ¹H NMR (CDCl₃, 500 MHz) δ: 0.61 (t, *J* = 7.5, 3 H), 0.73 (t, *J* = 7.5, 3 H), 1.28-1.31 (m, 5 H), 1.38 (s, 3 H), 1.40 (d, *J* = 6.3 Hz, 1 H), 1.40-1.45 (m, 1 H), 1.85 (d, *J* = 6.3, 1 H), 3.96-3.99 (2 × d, AB system, *J* = 8.3 Hz, 2 H), 5.46 (bs, 1 H), 7.18-7.27 (m, 9 H), 7.63-7.64 (m, 6 H). ¹³C NMR (CDCl₃, 125 MHz) δ: 7.5, 7.9, 27.8, 28.5, 29.3, 30.1, 30.8, 47.3, 67.3, 72.1, 75.7, 79.5, 126.9, 127.6, 129.6, 143.7, 165.7. ESI-MS *m/z* (rel. int): 491 [M+Na]⁺ (100). FT-IR (KBr) cm⁻¹: 3508, 3314, 3060, 2967, 1667, 1490, 1448, 1164, 709.

(2*R*,3*S*)-3-[2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]pentan-3-ol: (presumed er: 99:1); [α]_D²⁰ (c = 0.75, CHCl₃) = – 46.9.

(2*R,3*S**,1'*R**)-4-Bromophenyl-[3-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]methanol 6b**, (80%), white solid. mp: 70 – 73 °C. ¹H NMR (CDCl₃, 500 MHz) δ: 1.36 (s, 6 H), 1.75 (dd, *J* = 6.3, 4.4 Hz 1 H), 1.98 (d, *J* = 6.3 Hz, 1 H), 4.02 (bs, 2 H), 4.50 (bs, 1H), 5.00 (d, *J* = 4.4 Hz, 1 H), 7.15-7.34 (2 × d, AB system, *J* = 8.5 Hz, 4 H), 7.18-7.27(m, 9 H), 7.54-7.55 (m, 6 H). ¹³C NMR(CDCl₃, 125 MHz) δ: 28.3, 28.4, 31.5, 45.9, 67.4, 70.5, 75.1, 79.4, 121.1, 127.0, 127.1, 127.9, 129.3 131.2, 141.0, 143.3, 164.2. ESI/MS *m/z* (rel. int): 591 [M+ Na]⁺ (100). FT-IR (KBr) cm⁻¹: 3418, 2959, 2952, 1659, 1488, 1451, 1362, 1255, 1193, 1008, 708.

(2*R*,3*S*,1'*R*)-4-Bromophenyl-3-[(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]methanol: er: 99:1; [α]²⁰_D (c = 0.4, CHCl₃) = -11.

(2*R,3*S**,1'*R**)-[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]phenylmethanol 6c**: 80%, white solid, mp: 58 – 60 °C. ¹H NMR (CDCl₃, 500 MHz) δ: 1.35 (s, 3 H), 1.38 (s, 3 H), 1.88 (dd, *J* = 6.2, 5.2 Hz, 1 H), 2.05 (d, *J* = 6.2 Hz, 1 H), 4.00 (bs, 1 H), 4.03-4.06 (2 × d, AB system, *J* = 8.1 Hz, 2 H), 5.12 (d, *J* = 5.2, 1 H), 7.21-7.30 (m, 13 H), 7.61-7.62 (m, 6 H). ¹³C NMR (CDCl₃, 150 MHz) δ: 28.4, 28.4, 31.8, 46.0, 67.4, 71.5, 75.2, 79.4, 126.2, 127.0, 127.4, 127.8, 128.2, 129.4, 141.7, 143.5, 164.1. ESI/MS *m/z* (rel. int): 511 [M+Na]⁺ (100). FT-IR (film) cm⁻¹: 3283, 3059, 2967, 2928, 1661, 1596, 1491, 1449, 1366, 1265, 1191, 1039, 909, 737, 708, 637.

(2*R*,3*S*,1'*R*)-3-[(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]phenylmethanol: (presumed er: 99:1); [α]²⁰_D (c = 0.55, CHCl₃) = - 45.

(2*R,3*S**,1'*R**)-[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]-4-methoxyphenylmethanol 6d**: 70%, white solid, mp: 68 – 70 °C. ¹H NMR (CDCl₃, 500 MHz) δ: 1.30 (s, 3 H), 1.34 (s, 3 H), 1.83 (dd, *J* = 6.2, 5.4 Hz 1 H), 2.00 (d, *J* = 6.2 Hz, 1 H), 3.40 (bs, 1H), 3.72 (s, 3 H), 3.98-4.01 (2 × d, AB system, *J* = 7.9 Hz, 2 H), 5.04 (d, *J* = 5.4 Hz, 1 H), 6.75-7.27 (m, 13 H), 7.58-7.60 (m, 6 H). ¹³C NMR (CDCl₃, 100 MHz) δ: 28.3, 28.3, 31.7, 45.9, 55.2, 67.3, 71.3, 75.0, 79.3, 113.5, 126.9, 127.3, 127.7, 129.3, 133.8, 143.4, 158.8. ESI/MS *m/z* (rel. int): 519 [M+H]⁺ (100). FT-IR (KBr) cm⁻¹: 3284, 3055, 2963, 2930, 1659, 1611, 1513, 1448, 1248, 1174, 1032, 830, 709.

(2*R*,3*S*,1'*R*)-3-[(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]-4-methoxyphenylmethanol: (presumed er: 99:1); [α]²⁰_D (c = 0.5, CHCl₃) = - 11.

(2*R,3*S**,1'*S*')-[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]furan-2-**

ylmethanol 6e: 70%, white solid, mp: 87 – 90 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 1.31 (s, 3 H), 1.32 (s, 3 H), 1.98-2.06 (m, 2 H), 3.95-3.99 (2 × d, AB system *J* = 7.9 Hz, 2 H), 5.14 (d, *J* = 4.0 Hz, 1 H), 6.13-6.15 (m, 1 H), 6.22-6.23 (m, 1 H), 7.19-7.28 (m, 10 H), 7.57-7.58 (m, 6 H). ¹³C NMR (CDCl₃, 100 MHz) δ: 28.2, 31.1, 43.0, 66.4, 67.3, 75.0, 79.3, 106.3, 110.0, 126.9, 127.7, 129.4, 141.7, 143.4, 154.5, 164.0. ESI/MS *m/z* (rel. int): 501 [M+Na]⁺ (100). FT-IR (KBr)cm⁻¹ : 3333, 2967, 1660, 1448, 1369, 1181, 1265, 034, 1013.

(2*R*,3*S*,1'*S*')-[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]furan-2-ylmethanol:

(presumed er: 99:1); [α]²⁰_D (c = 0.4, CHCl₃) = – 18.4.

(2*R,3*S**,1'*R*')-[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]-2,2-**

dimethylpropan-1-ol 6f: 75%, white solid, mp: 137 – 140 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 0.76 (s, 9 H), 1.33 (s, 3 H), 1.35 (s, 3 H), 1.64 (dd, *J* = 6.6, 6.2 Hz, 1 H), 2.04 (d, *J* = 6.2 Hz, 1 H), 2.74 (bs, 1 H), 3.54 (d, *J* = 6.6 Hz, 1 H), 3.99-4.06 (2 × d, AB system, *J* = 7.7 Hz, 2 H), 7.18-7.29 (m, 9 H), 7.59-7.61 (m, 6 H). ¹³C NMR (CDCl₃, 100 MHz) δ: 25.9, 26.0, 28.2, 28.4, 32.8, 42.1, 67.3, 75.4, 75.9, 79.2, 126.9, 126.7, 129.4, 143.5, 163.8. ESI-MS *m/z* (rel. int): 491 [M+Na]⁺ (100). FT-IR (KBr) cm⁻¹ : 3384, 3059, 2962, 1664, 1490, 1448, 1364, 1254, 1165, 1003, 955, 709.

(2*R*,3*S*,1'*R*')-[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]-2,2-

dimethylpropan-1-ol: er: 99:1; [α]²⁰_D (c = 1.5, CHCl₃) = -53.5.

(2*R,3*S*')-[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]-1-phenylethanol 6g:**

mixture of diastereomers (dr: 1/1) separated by flash chromatography (petroleum ether/AcOEt 9/1). First eluted diastereomer: 25%, colourless oil, ¹H NMR (CDCl₃, 400 MHz) δ: 1.0 (s, 3 H), 1.20 (s, 3 H), 1.47 (s, 3 H), 1.86 (d, *J* = 5.9 Hz, 1 H), 2.02 (d, *J* = 5.9 Hz, 1H), 3.34-3.72 (2 × d, AB system, *J*=8.0 Hz, 2 H), 6.42 (b.s., exchanges with D₂O, 1 H), 7.11 -7.33 (m, 14 H), 7.70 -7.72 (m, 6 H). ¹³C NMR δ: 26.9, 28.2, 30.8, 32.8, 48.5, 66.9, 71.3, 75.7, 79.1, 124.8, 126.2, 126.3, 127.0, 127.6, 129.6, 143.7, 149.1, 164.8. ESI-MS *m/z* (rel. int): 525 [M+Na]⁺ (100). FT-IR (film) cm⁻¹: 3261, 3059, 2973, 2927, 1667, 1596, 1490, 1448, 1365, 1258, 1167, 1096, 1061, 1024, 950, 710.

(2*R*,3*S*')-[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]-1-phenylethanol

(presumed er: 99:1); [α]²⁰_D (c = 0.5, CHCl₃) = – 76.8.

(2*R,3*S**)-[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]-1-phenylethanol 6g**

Second eluted diastereomer: 25%, colourless oil. ¹H NMR (CDCl₃, 400 MHz) δ: 1.39 (s, 6 H), 1.44 (s, 3 H), 1.82 (d, *J* = 6.0 Hz, 1 H), 1.93 (d, *J* = 6.0 Hz, 1 H), 4.03 -4.05 (2 × d, AB system, *J* = 8.0 Hz, 2 H), 6.49 (b.s., exchanges with D₂O, 1 H), 7.08-7.21 (m, 14 H), 7.37 -7.42 (m, 6 H). ¹³C NMR δ: 27.9, 28.3, 29.6, 30.2, 50.5, 67.4, 71.4, 75.3, 79.6, 124.9, 125.1, 126.7, 127.7, 129.3, 129.4, 143.2, 147.4, 165.6. ESI-MS *m/z* (rel. int): 525 [M+Na]⁺ (100). FT-IR (film)cm⁻¹: 3263, 3058, 2968, 2927, 1668, 1493, 1448, 1265, 1165, 1067, 909, 702.

(2*R*,3*S*)-[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-tritylaziridin-2-yl]-1-phenylethanol

(presumed er: 99:1); [α]_D²⁰ (c = 0.65, CHCl₃) = - 68.7.

General procedure for the lithiation-trapping sequence of aziridines 3b:

To a solution of the aziridines **3b** (1 mmol) and TMEDA (2.0 mmol) in 10 mL of dry THF, at -98°C and under N_2 , *s*-BuLi (2.0 mmol of a 1.4 M cyclohexane solution) was added dropwise. The resulting yellow mixture was stirred for 2 h at this temperature before quenching with the electrophile (neat if liquid or diluted in 2 mL of THF if solid). The reaction mixture was warmed up to room temperature and a solution of sat. aq. NH_4Cl (3 mL) was added, the mixture poured in 20 mL of water and extracted with Et_2O (3×10 mL). The combined organic layers were dried (Na_2SO_4) and the solvent evaporated in *vacuo*. The crude was purified by flash chromatography on silica gel (AcOEt/Petroleum Ether) to furnish aziridines **8a-c** and **9a-c**.

α and β Deuterated aziridine 8a and 9a: 90%, 94 % D, colourless oil. ^1H NMR (CDCl_3 , 600 MHz) δ : 1.26 (s, 3 H), 1.29 (s, 3 H), 1.43 (s, 3 H), 1.49 (s, 3 H), 1.65 (s overlapping d, 1 H), 2.03 (s, 0.33 H), 2.22 (d, $J = 6.4$ Hz, 0.67 H), 3.90-3.99 (2 $\times$ d, AB system, $J = 7.7$ Hz, 2 H), 7.21-7.32 (m, 3 H), 7.43 (d, $J = 8.2$ Hz, 2 H). ^{13}C NMR (CDCl_3 , 150 MHz) δ : 25.7, 27.3, 27.4, 28.2, 28.2, 28.3, 58.9, 67.0, 79.2, 126.6, 126.8, 127.9, 143.3, 164.1. ESI-MS m/z (rel. int): 260 $[\text{M}+\text{H}]^+$ (100). FT-IR (film) cm^{-1} : 2894, 1660, 1518, 1495, 1462, 1384, 1363, 1301, 1229, 1102, 1031, 765.

($\pm$)-2-[2-Ethyl-1-(2-phenylpropan-2-yl)aziridin-2-yl]-4,4-dimethyl-4,5-dihydrooxazole **8b:** 18%, yellow oil. ^1H NMR (CDCl_3 , 600 MHz) δ : 0.86 (t, $J = 7.1$ Hz, 3 H), 1.16 (s, 3 H), 1.19 (s, 3 H), 1.34 (s, 3 H), 1.41 (s, 3 H), 1.26-1.30 (m, 1 H), 1.79 (s, 1 H), 2.03-2.09 (m, 1 H), 2.37 (s, 1 H), 3.72-3.77 (2 $\times$ d, AB system, $J = 8.2$, 2 H), 7.16-7.27 (m, 3 H), 7.46 (d, $J = 8.0$ Hz, 2 H). ^{13}C NMR (CDCl_3 , 150 MHz) δ : 10.0, 27.3, 28.6, 28.6, 32.1, 41.0, 58.9, 66.8, 78.7, 125.8, 126.2, 127.8, 148.7, 164.1. ESI-MS m/z (rel. int): 287 $[\text{M}+\text{H}]^+$ (100). FT-IR (film) cm^{-1} : 2967, 2928, 1654, 1495, 1462, 1446, 1363, 1252, 1178.

(2*R,3*R**)-2-[3-Ethyl-1-(2-phenylpropan-2-yl)aziridin-2-yl]-4,4-dimethyl-4,5-dihydrooxazole **9b**:** 36%, yellow oil. ^1H NMR (CDCl_3 , 600 MHz) δ : 0.92 (t, $J = 7.4$ Hz, 3 H), 1.21 (s, 3 H), 1.23 (s, 3 H), 1.36 (s, 3 H), 1.45 (s, 3 H), 1.48-1.54 (m, 1 H), 1.54-1.61 (m, 1 H), 1.71 (q, $J = 6.6$ Hz, 1 H), 2.17 (d, $J = 6.6$ Hz, 1 H), 3.86-3.92 (2 $\times$ d, AB system, $J = 8.0$ Hz, 2 H), 7.17-7.27 (m, 3 H), 7.40 (d, $J = 7.6$ Hz, 2 H). ^{13}C NMR (CDCl_3 , 150 MHz) δ : 11.9, 21.8, 25.4, 28.0, 28.3, 28.4, 32.6, 40.7, 58.6, 67.0, 79.0, 126.7, 126.7, 127.7, 143.7, 163.6. ESI-MS m/z (rel. int): 287 $[\text{M}+\text{H}]^+$ (100). FT-IR (film) cm^{-1} : 2967, 2928, 1653, 1495, 1462, 1446, 1363, 1252, 1175.

2-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-(2-phenylpropan-2-yl)aziridin-2-ylphenylmethanol 8c: 22%, (inseparable mixture of diastereoisomers 60:40), ¹H NMR (CHCl₃, 600 MHz) δ: 0.83 (s, 3 H, major), 0.89 (s, 3 H, minor), 0.95 (s, 3 H, major), 0.98 (s, 3 H, minor), 1.34 (s, 3 H, major), 1.35 (s, 3 H, minor), 1.46 (s, 3 H, minor), 1.51 (s, 3 H, major), 2.13 (s, 1 H, major), 2.23 (s, 1 H, minor), 2.38 (s, 1 H, minor), 2.49 (s, 1 H, major), 3.35-3.53 (2 × d, AB system, *J* = 8.2 Hz, 2 H, major), 3.56-3.59 (2 × d, AB system, *J* = 8.2 Hz, 2 H, minor), 4.19 (bs, 1 H, minor), 4.32 (s, 1 H, major), 4.61 (bs, 1 H, major), 4.99 (s, 1 H, minor), 7.11-7.27 (m, 6 H, major + minor), 7.40 (d, *J* = 7.5 Hz, 2 H, minor), 7.47 (d, *J* = 7.5 Hz, 2 H, major), ¹³C NMR (CHCl₃, 150 MHz) δ: 26.9, 27.1, 27.3, 27.5, 27.7, 27.8, 27.9, 28.2, 29.7, 32.2, 43.4, 43.6, 58.7, 59.0, 67.1, 70.8, 78.6, 78.67, 125.5, 126.1, 126.1, 126.5, 126.6, 127.1, 127.2, 127.7, 127.9, 128.0, 128.1, 141.1, 147.1, 147.4, 162.1 (major + minor). ESI-MS *m/z* (rel. int): 365 [M+H]⁺ (100). FT-IR (film) cm⁻¹: 3369, 2972, 1651, 1449, 1252, 1175, 1050.

[3-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-1-(2-phenylpropan-2-yl)aziridin-2-yl]phenylmethanol 9c: 44%, yellow oil. ¹H NMR (CHCl₃, 400 MHz) δ: 1.19 (s, 3 H), 1.22 (s, 3 H), 1.32 (s, 3 H), 1.46 (s, 3 H), 2.03 (dd, *J* = 6.2, 5.9 Hz, 1 H), 2.24 (d, *J* = 6.2 Hz, 1 H), 3.87-3.92 (2 × d, AB system, *J* = 8.4 Hz, 2 H), 4.73 (d, *J* = 5.9 Hz, 1 H), 7.21 -7.26 (m, 3 H), 7.34 (d, *J* = 8.3 Hz, 2 H). ¹³C NMR (CDCl₃, 100 MHz) δ: 25.5, 27.8, 28.3, 32.8, 45.5, 58.8, 67.2, 70.5, 79.2, 125.7, 126.7, 127.0, 127.3, 128.0, 128.3, 142.0, 142.8, 163.3. ESI-MS *m/z* (rel. int): 365 [M+H]⁺ (100). FT-IR (film) cm⁻¹: 3194, 2966, 1644, 1446, 1371, 1251, 1050, 994.

General procedure for the lithiation-trapping sequence of aziridines **3c**:

To a solution of the aziridines **3c** (1 mmol) in 10 mL of dry THF, at $-98\text{ }^{\circ}\text{C}$ and under N_2 , *n*-BuLi (2.0 mmol of a 2.0 M cyclohexane solution) was added dropwise. The resulting reddish mixture was stirred for 4 h at this temperature before quenching with the electrophile (neat if liquid or diluted in 2 mL of THF if solid). The reaction mixture was warmed up to room temperature and a solution of sat. aq. NH_4Cl (3 mL) was added, the mixture poured in 20 mL of water and extracted with Et_2O ($3 \times 10\text{ mL}$). The combined organic layers were dried (Na_2SO_4) and the solvent evaporated in *vacuo*. The crude was purified by flash chromatography on silica gel (AcOEt/Petroleum Ether) to furnish aziridines **10a-c**.

(±)-2-(1-Benzyl-2-deuterioaziridin-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 10a: 95%, 97% D colourless oil, mp: $40\text{--}42\text{ }^{\circ}\text{C}$. ^1H NMR (CDCl_3 , 500 MHz) δ : 1.26 (s, 3 H), 1.28 (s, 3 H), 1.70 (s, 1H), 2.24 (s, 1H), 3.35-3.77 ($2 \times \text{d}$, AB system, $J = 13.5\text{ Hz}$, 2 H), , 3.91-3.98 ($2 \times \text{d}$, AB syistem, $J = 8.1\text{ Hz}$, 2 H), 7.24-7.36 (m, 5 H). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 28.1, 28.1, 33.3, 34.1, 63.9, 67.0, 79.1, 127.0, 127.9, 128.1, 137.7. ESI-MS: 232 $[\text{M}+\text{H}]^+$. FT-IR cm^{-1} : 2969, 1665, 1454, 1351, 1301, 1252, 1199, 1004, 736.

(±)-2-(1-Benzyl-2-methylaziridin-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 10b: 50%, (mixture of two slowly equilibrating invertomers 60:40), yellow oil. ^1H NMR (CDCl_3 , 600 MHz, $T = 273\text{ K}$) δ : 1.16 (s, 3 H, major), 1.17 (s, 3 H, major), 1.22 (s, 3 H, minor), 1.23 (s, 3 H, minor), 1.44 (s, 3 H, major), 1.48 (s, 3 H, minor), 1.53 (s, 1 H, minor), 1.92 (s, 1 H, major), 2.19 (s, 1 H, major), 2.42 (s, 1 H, minor), 3.56-3.94 ($2 \times \text{AB system}$, 4 H, major + $2 \times \text{AB system}$, 4 H, minor), 7.16-7.29 (m, 10 H, major + minor). ^{13}C NMR δ : 12.8, 21.6, 28.2, 28.5, 36.0, 37.0, 39.8, 40.0, 56.4, 56.6, 67.1, 67.2, 78.9, 79.2, 126.7, 127.2, 127.5, 128.2, 139.1, 139.3, 163.4, 166.5. ESI-MS m/z (rel. int): 245 $[\text{M}+\text{H}]^+$ (100). FT-IR (film) cm^{-1} : 2969, 1654, 1453, 1364, 1120.

(±)-2-(1-Benzyl-2-ethylaziridin-2-yl)-4,4-dimethyl-4,5-dihydrooxazole 10c: 70%, (mixture of two slowly equilibrating invertomers 90:10), yellow oil. ^1H NMR (CDCl_3 , 400 MHz, $T = 273\text{ K}$) δ : 0.92 (t, $J = 7.53\text{ Hz}$, 3 H, major), 1.04 (t, $J = 7.53\text{ Hz}$, 3 H, minor), 1.22 (s, 3 H, major), 1.22 (s, 3 H, major) 1.24, (s, 3 H, minor), 1.25 (s, 3 H, minor), 1.25-1.30 (m, 1 H, major), 1.48 (s, 1 H, minor), 1.65-1.73 (m, 1 H, minor), 1.91 (s, 1 H, major), 1.93-1.97 (m, 1 H, minor), 2.13 (s, 1 H, major), 2.19-2.26 (m, 1 H, major), 2.41 (s, 1 H, minor), 3.48-3.78 ($2 \times \text{d}$, AB system, $J = 13.87\text{ Hz}$, 2H, major), 3.70-3.81 ($2 \times \text{d}$, AB system, $J = 14.27\text{ Hz}$, 2 H, minor), 3.83-3.88 ($2 \times \text{d}$, AB system, $J = 7.93\text{ Hz}$, 2 H, major), 3.87-3.93 ($2 \times \text{d}$, AB system, $J = 7.93\text{ Hz}$, 2 H, minor), 7.17-7.37 (m, 10 H, major + minor). ^{13}C NMR (CDCl_3 , 125 MHz) δ : 10.0, 28.4, 28.6, 28.7, 38.4, 45.2, 57.0, 67.4, 78.9, 126.8, 127.8, 128.3, 139.5, 162.8. ESI-MS m/z (rel. int): 259 $[\text{M}+\text{H}]^+$ (100). FT-IR (film) cm^{-1} : 2967, 1650, 1445, 1122, 970.

General procedure for the preparation of 2,3-aziridino- γ -butyrolactones 7a,b:

To a solution of hydroxyalkylated aziridines **6** (1 mmol) in dioxane/H₂O 4:1 (5 mL) was added CF₃COOH (0.1 mmol) at room temperature and the resulting solution stirred for 48 h (TLC monitoring). After this time 10 mL of an aqueous solution (10 %) of NaHCO₃ was added and then extracted with CH₂Cl₂ (3 x 10mL). The combined organic layers were dried (Na₂SO₄) and the solvent evaporated in *vacuo*. The crude was purified by flash chromatography (AcOEt/hexane) to get the lactones **7**.

(1R*,5S*)-4,4-Diethyl-6-trityl-3-oxa-6-aza-bicyclo[3.1.0]hexan-2-one 7a: 30%, colourless oil. ¹H NMR (500 MHz, CDCl₃), δ : 0.75(t, J = 7.3 Hz, 3 H), 0.77 (t, J = 7.3 Hz, 3 H), 1.46-1.59 (m, 2 H), 1.93-2.1 (m, 2 H), 2.37-2.40 (2 $\times$ d, AB system, J = 4.3Hz, 2 H), 7.20-7.29 (m, 9 H), 7.45-7.47 (m, 6 H). ¹³C NMR (125 MHz, CDCl₃), δ : 8.6, 8.8, 26.2, 28.7, 36.7, 43.3, 74.5, 89.1, 127.2, 127.8, 127.9, 129.2, 143.0, 143.2, 146.8, 173.2. ESI-MS m/z (rel. int): 443 [M+Na]⁺. FT-IR (film) cm⁻¹: 2971, 1771, 1490, 1447, 704.

(1R*,4S*,5S*)-4-(4-Bromophenyl)-6-trityl-3-oxa-6-aza-bicyclo[3.1.0]hexan-2-one 7b: 65%, yellow oil. ¹H NMR (600 MHz, CDCl₃), δ : 2.62 (d, J =3.8, 1 H), 3.05 (dd, J = 3.8, 2.7 Hz, 1 H), 5.58 (d, J = 2.7 Hz, 1 H), 7.26-7.68 (m, 19 H). ¹³C NMR (150 MHz, CDCl₃), δ : 30.0, 41.0, 74.3, 79.5, 122.3, 127.2, 127.3, 127.6, 127.8, 127.9, 129.0, 131.8, 135.4, 142.9, 172.6. ESI-MS m/z (rel. int): 518 [M+Na]⁺ (100). FT-IR (film) cm⁻¹: 2923, 2852, 1771, 1489, 1196, 1051, 804, 703.

(1R*,4R*,5S*)-4-(4-Bromophenyl)-6-trityl-3-oxa-6-aza-bicyclo[3.1.0]hexan-2-one diast-7b: 40%, white oil. ¹H NMR (500 MHz, CDCl₃), δ : 2.58 2.63 (2 $\times$ d, AB system, J = 4.4 Hz, 2 H), 5.65 (s, 1 H), 7.08-7.09 (m, 2 H), 7.26-7.34 (m, 11 H), 7.46-7.49 (m, 6 H). ¹³C NMR (150 MHz, CDCl₃), δ : 36.1, 42.8, 73.8, 82.2, 125.0, 127.0, 128.0, 132.3, 143.5, 147.1, 178.2. fid. ESI-MS m/z (rel. int): 518 [M+Na]⁺ (100). FT-IR (film) cm⁻¹: 2920, 1783, 1446, 1001.

The deuterium incorporation was determined by ^1H NMR analysis on the crude reaction mixture and by ESI-MS on the molecular ion and after correction of the amount of the non deuterated aziridine eventually present in the sample.

Sample preparation for ESI-MS analysis:

The crude (0.5 mg) was dissolved in 1 mL of MeOH and 10 μL of formic acid were added. The resulting solution was directly injected into the ESI-MS analyzer.

Comparison of ^1H NMR and ESI-MS spectra of deuterated and non-deuterated aziridine **3a**.

Comparison of ^1H NMR and ESI-MS spectra of deuterated and non-deuterated aziridine **3b**.

Comparison of ^1H NMR and ESI-MS spectra of deuterated and non-deuterated aziridine **3c**.

Determination of the enantiomeric ratio

The enantiomeric ratio has been determined by comparison with a pure racemic sample by ^1H NMR of the aziridinium salt obtained with a chiral Mosher's acid or by HPLC on chiracel OD-H column (typical mobile phase hexane/2-propanol 90:10, 1 mL/min) with an UV detector at 259 nm.

NOESY 2D of Aziridine **3a**: