

## Supporting information

**General:** All NMR experiments were done on a Unity 400 MHz spectrometer (400 MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$ ), and chemical shifts are given in ppm relative to TMS. For the photo-initiated radical cyclizations a micro photochemical reaction assembly as designed by J. H. Penn and R. D. Orr<sup>1</sup> from Aldrich was used. A borosilicate glass immersion well was employed to exclude wavelengths lower than 300 nm. Except for the radical cyclizations (performed under an argon atmosphere), all reactions were carried out under an atmosphere of dry nitrogen. Coupling constants (some of them were measured using J doubling<sup>2</sup>) are all given in Hz. The assignment of pyrrolidine stereochemistry was based on NOE difference and noesy experiments. *Cis/trans*-ratios were determined by integration in crude  $^1\text{H}$  NMR spectra.

**Solvents:** Anhydrous solvents were used in all reactions. Drying was accomplished by refluxing over sodium (THF, diethyl ether) or calcium hydride (dichloromethane, benzene) before distillation.

**Materials:** *N*-Allyl-2-aziridinecarbonitrile was synthesised according to literature.<sup>3</sup> Tri-*n*-butyltin hydride was made as described in the literature,<sup>4</sup> and stored in ampoules. All other chemicals were purchased from Lancaster or Aldrich.

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<sup>1</sup> Penn, J. H.; Orr, R. D. *J. Chem. Ed.* **1989**, 66, 86.

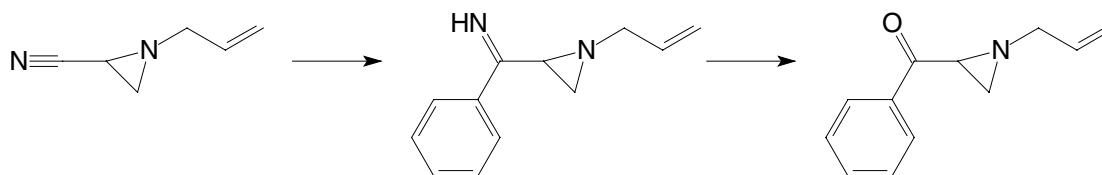
<sup>2</sup> McIntyre, R.; Freeman, R. *J. Magn. Reson.* **1992**, 96, 425. del Rio-Portilla, F.; Blechta, V.; Freeman, R. *J. Magn. Reson.* **1994**, A 111, 132.

<sup>3</sup> U.S. patent 4,321,197 (1983).

<sup>4</sup> Kuivila, H. G.; Beumel, O. F. *J. Am. Chem. Soc.* **1961**, 83, 1246.

**Typical procedure for addition of an organolithium reagent to 2-aziridinecarbonitrile:**

**1-Allyl-2-benzoyl-aziridine (5a) (Procedure A):**



Phenyllithium (1.1 mL 1.8 M, 2 mmol) in cyclohexane/ether (70/30) was added to diethyl ether (5 mL) and cooled to  $-78^{\circ}\text{C}$ . Neat *N*-allyl-2-aziridinecarbonitrile (108 mg, 1 mmol) was added dropwise and the solution was stirred until no starting material could be spotted on TLC. The reaction mixture was diluted with ether and extracted with saturated  $\text{NH}_4\text{Cl}$  (aq.). The ether phase was dried over NaOH pellets and evaporated. In case of aliphatic organolithium reagents, this treatment was enough to cause hydrolysis of the imines. With aromatic organolithium reagents the imines were efficiently hydrolysed by refluxing with  $\text{LiOH}\cdot\text{H}_2\text{O}$  (252 mg, 6 mmol) in  $\text{MeOH}/\text{H}_2\text{O}$  (1:1) for 1 h. The crude material was purified on silica gel (ether:pentane = 3:1) to yield 169 mg (90%) of the title compound.

**1-Allyl-2-benzoyl-aziridine (5a) from Grignard addition (Procedure B):**

Phenylmagnesium bromide (8.6 mmol) was prepared according to standard procedures in THF (20 mL) and cooled to  $0^{\circ}\text{C}$  and TMEDA (12.1 g, 104 mmol) was added to keep the reagent in solution. Neat *N*-allyl-2-aziridinecarbonitrile (462 mg, 4.27 mmol) was added dropwise. Work-up according to the above procedure afforded the title compound in 92% yield. In the reaction with isopropylmagnesium bromide, it was found that addition of a catalytic amount of  $\text{CuBr}^5$  (0.1 equivalents) to the Grignard reagent before the aziridine was introduced gave a cleaner and higher yielding reaction.

<sup>5</sup> Hweiberth, F. J.; Hall, S. S. *J. Org. Chem.* **1987**, 52, 3901.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.82 (dd,  $J = 1.5, 6.5$ , 1H), 2.34 (dd,  $J = 1.5, 3.1$ , 1H), 2.94 (dd,  $J = 3.1, 6.4$ , 1H), 3.02 (tdd,  $J = 1.4, 5.9, 14.0$ , 1H), 3.17 (tdd,  $J = 1.5, 5.5, 14.0$ , 1H), 5.15 (tdd,  $J = 1.4, 1.7, 10.4$ , 1H), 5.26 (tdd,  $J = 1.4, 1.7, 17.2$ , 1H), 5.98 (dddd,  $J = 5.5, 5.9, 10.4, 17.2$ , 1H), 7.45-7.50 (several peaks, 2H), 7.58 (m, 1H), 8.02-8.06 (several peaks, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  36.4, 40.5, 63.1, 117.0, 128.2, 128.5, 133.2, 134.3, 136.7, 196.0.

**1-Allyl-2-thienoyl-aziridine (5b):** Yield 68% (Procedure A),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.72 (dd,  $J = 1.3, 6.5$ , 1H), 2.24 (dd,  $J = 1.4, 3.1$ , 1H), 2.67 (dd,  $J = 3.2, 6.6$ , 1H), 2.91 (tdd,  $J = 1.5, 5.8, 14.1$ , 1H), 3.05 (tdd,  $J = 1.6, 5.4, 14.1$ , 1H), 5.05 (tdd,  $J = 1.4, 1.7, 10.4$ , 1H), 5.17 (qd,  $J = 1.7, 17.2$ , 1H), 5.87 (dddd,  $J = 5.4, 5.8, 10.4, 17.2$ , 1H), 7.05 (dd,  $J = 3.8, 4.9$ , 1H), 7.57 (dd,  $J = 1.2, 5.0$ , 1H), 7.89 (dd,  $J = 1.2, 3.8$ , 1H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  36.0, 41.6, 62.5, 116.7, 127.8, 132.6, 134.0 (2 peaks), 142.1, 188.9.

**1-Allyl-2-(hexanoyl)-aziridine (5c):** Yield 60% (Procedure B),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.85 (t,  $J = 6.9$ , 3H), 1.18-1.33 (several peaks, 4H), 1.48-1.59 (several peaks, 2H), 1.63 (dd,  $J = 2.7, 5.2$ , 1H), 2.08-2.11 (several peaks, 2H), 2.27 (ddd,  $J = 6.8, 8.2, 14.9$ , 1H), 2.27 (ddd,  $J = 6.8, 8.3, 15.0$ , 1H), 2.85 (dddd,  $J = 1.3, 1.6, 5.9, 14.0$ , 1H), 3.00 (dddd,  $J = 1.4, 1.7, 5.6, 14.0$ , 1H), 5.12 (tdd,  $J = 1.3, 1.7, 10.3$ , 1H), 5.18 (qd,  $J = 1.7, 17.2$ , 1H), 5.89 (dddd,  $J = 5.6, 5.9, 10.5, 17.2$ , 1H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  13.9, 22.4, 23.1, 31.3, 34.7, 38.0, 44.4, 62.7, 117.0, 134.3, 208.8.

**1-Allyl-2-(2-methylpropanoyl)-aziridine (5d):** Yield 52% (Procedure B),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.03 (d, 6.9, 3H), 1.06 (d, 6.9, 3H), 1.61 (dd,  $J = 1.3, 6.7$ , 1H), 2.06 (dd,  $J = 1.3, 3.2$ , 1H), 2.15 (dd,  $J = 3.1, 6.6$ , 1H), 2.70 (sep,  $J = 6.9$ , 1H), 2.81 (tdd,  $J = 1.3, 6.1, 13.9$ , 1H), 3.02 (tdd,  $J = 1.5, 5.6, 13.8$ , 1H), 5.08 (tdd,  $J = 1.3, 1.8, 10.4$ , 1H), 5.15 (tdd,  $J = 1.3, 1.7, 17.2$ , 1H), 5.87 (dddd,  $J = 5.6, 6.1, 10.4, 17.2$ , 1H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  17.8, 18.3, 35.1, 37.3, 42.3, 62.8, 117.0, 134.2, 211.4.

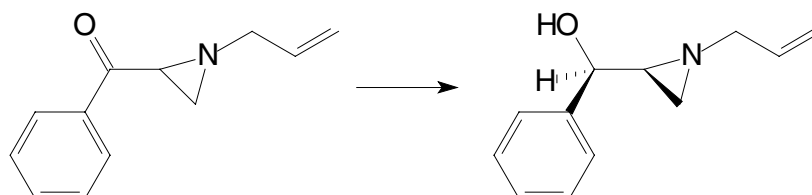
**1-Allyl-2-[3-(1,3-dioxolan-2-yl)-propanoyl]-aziridine (5e):** Yield 73% (Procedure B),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.66 (dd,  $J = 1.8, 5.9$ , 1H), 1.94 (ddd,  $J = 0.6, 4.4, 7.4$ , 1H), 1.96 (dd,  $J = 4.4, 7.4$ , 1H), 2.12-2.17 (several peaks, 2H), 2.44 (ddd,  $J = 7.2, 7.7, 14.9$ , 1H), 2.60 (ddd,  $J = 6.9, 8.0, 14.8$ , 1H), 2.89 (dddd,  $J = 1.3, 1.6, 5.9, 14.0$ , 1H), 3.00 (dddd,  $J = 1.4, 1.7, 5.6, 14.0$ , 1H),

3.79-3.88 (several peaks, 2H), 3.90-3.99 (several peaks, 2H), 4.90 (t,  $J = 4.4$ , 1H), 5.14 (tdd,  $J = 1.4$ , 1.7, 10.3, 1H), 5.20 (qd,  $J = 1.7$ , 17.2, 1H), 5.90 (dddd,  $J = 5.6$ , 5.7, 10.4, 17.2, 1H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  27.0, 31.8, 34.7, 44.2, 62.5, 64.7, 103.0, 116.8, 134.1, 207.5 (one C missing/overlapping).

**Typical procedure for reduction of aziridineketones 5 to the corresponding *erythro* aziridinealcohols 6:**

**1-Allyl-*erythro*-2-(1-hydroxy-1-phenylmethyl)-aziridine (6a):**



1-Allyl-2-benzoyl-aziridine (1.82 g, 9.72 mmol) was dissolved in MeOH (60 mL) and stirred with  $\text{ZnBr}_2$  (2.41 g, 10.7 mmol) for 0.5 h. The mixture was heated to reflux and  $\text{NaBH}_4$  (0.552 g, 14.6 mmol) was added in portions (CAUTION! Gas evolution, foaming). The reaction was then left for 2 h and half of the MeOH was removed by evaporation. To the cooled (ambient temperature) solution was added ethylenediamine (2.9 mL, 43.7 mmol). The heterogeneous mixture was stirred for 1 h. Dichloromethane was added and the organic phase was extracted consecutively with NaOH (10% aq.),  $\text{NH}_3$  (28% aq.),  $\text{H}_2\text{O}$ , brine and dried with  $\text{K}_2\text{CO}_3$ . The crude product was purified by flash chromatography (pentane:acetone = 3:1) to yield 1.43 g (78%) of the title compound.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.27 (d,  $J = 6.4$ , 1H), 1.76 (td,  $J = 3.6$ , 6.4, 1H), 2.02 (dd,  $J = 0.6$ , 3.6, 1H), 2.87 (tdd,  $J = 1.4$ , 5.8, 14.1, 1H), 2.97 (tdd,  $J = 1.5$ , 5.6, 14.0, 1H), 3.68 (bs, 1H), 4.80 (d,  $J = 3.6$ , 1H), 5.09 (tdd,  $J = 1.3$ , 1.8, 10.4, 1H), 5.18 (qd,  $J = 1.7$ , 17.2, 1H), 5.85 (tdd,  $J = 5.7$ , 10.4, 17.2, 1H), 7.27 (m, 1H), 7.30-7.39 (several peaks, 4H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.3, 43.8, 62.0, 70.5, 116.4, 126.0, 127.5, 128.2, 134.8, 141.9.

**1-Allyl-erythro-2-(1-hydroxy-1-(2-thienyl)methyl)-aziridine (6b):** Yield 85%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.39 (d,  $J = 6.4$ , 1H), 1.88 (td,  $J = 3.5$ , 6.4, 1H), 2.08 (dd,  $J = 0.6$ , 3.6, 1H), 2.96 (tdd,  $J = 1.5$ , 5.8, 14.1, 1H), 3.02 (tdd,  $J = 1.5$ , 5.6, 14.1, 1H), 3.56 (bs, 1H), 5.10 (m, 1H), 5.13 (tdd,  $J = 1.4$ , 1.8, 10.4, 1H), 5.22 (qd,  $J = 1.7$ , 17.2, 1H), 5.90 (tdd,  $J = 5.7$ , 10.4, 17.2, 1H), 6.98 (dd,  $J = 3.5$ , 5.0, 1H), 7.05 (ddd,  $J = 0.7$ , 1.2, 3.5, 1H), 7.26 (dd,  $J = 1.2$ , 5.0, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.4, 43.4, 61.9, 66.8, 116.6, 124.2, 124.8, 126.4, 134.8, 145.3.

**1-Allyl-erythro-2-(1-hydroxyhexyl)-aziridine (6c):** Yield 88%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.84 (m, 3H), 1.22 (d,  $J = 6.4$ , 1H), 1.19-1.36 (several peaks, 6H), 1.39-1.47 (several peaks, 3H), 1.50 (td,  $J = 3.8$ , 6.4, 1H), 1.79 (d,  $J = 3.7$ , 1H), 2.84 (tdd,  $J = 1.5$ , 5.8, 14.0, 1H), 2.92 (tdd,  $J = 1.5$ , 5.6, 14.0, 1H), 3.62 (m, 1H), 5.16 (tdd,  $J = 1.3$ , 1.8, 10.3, 1H), 5.16 (qd,  $J = 1.7$ , 17.2, 1H), 5.86 (tdd,  $J = 5.7$ , 10.3, 17.2, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.0, 22.5, 25.0, 29.3, 31.9, 34.8, 42.6, 62.3, 68.6, 116.2, 135.0.

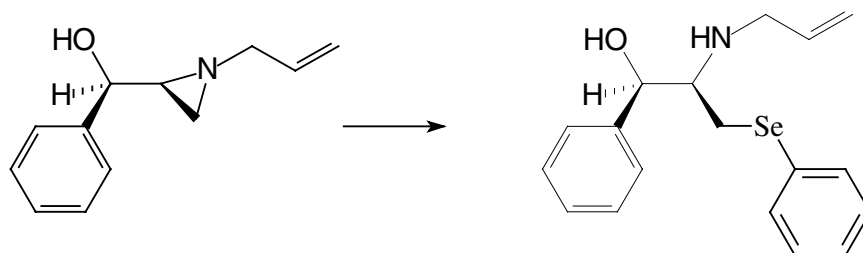
**1-Allyl-erythro-2-(1-hydroxy-2-methylpropyl)-aziridine (6d):** Yield 43%\*,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.94 (d, 6.9, 3H), 0.96 (d, 7.0, 3H), 1.26 (d,  $J = 6.4$ , 1H), 1.58 (td,  $J = 3.6$ , 6.4, 1H), 1.66 (dsep,  $J = 6.2$ , 6.9, 1H), 1.85 (dd,  $J = 0.6$ , 3.7, 1H), 2.78 (bs, 1H), 2.89 (tdd,  $J = 1.5$ , 5.7, 14.2, 1H), 2.95 (tdd,  $J = 1.6$ , 5.6, 14.2, 1H), 3.45 (ddd,  $J = 0.6$ , 3.4, 6.1, 1H), 5.10 (tdd,  $J = 1.4$ , 1.8, 10.4, 1H), 5.19 (qd,  $J = 1.8$ , 17.2, 1H), 5.88 (tdd,  $J = 5.7$ , 10.4, 17.2, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.2, 18.3, 29.1, 32.5, 40.7, 62.2, 72.8, 116.3, 135.0.

\* Work-up according to an inferior procedure excluding ethylenediamine.

**1-Allyl-erythro-2-[3-(1,3-dioxolan-2-yl)-1-hydroxypropyl]-aziridine (6e):** Yield 66%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.28 (d,  $J = 6.4$ , 1H), 1.55 (ddd,  $J = 3.7$ , 4.1, 6.3, 1H), 1.58 (dddd,  $J = 5.9$ , 8.2, 9.6, 13.8, 1H), 1.68 (dddd,  $J = 4.1$ , 5.8, 9.9, 13.8, 1H), 1.75-1.92 (several peaks, 2H), 1.85 (d,  $J = 3.7$ , 1H), 2.66 (bs, 1H), 2.88 (tdd,  $J = 1.6$ , 5.8, 14.0, 1H), 2.97 (tdd,  $J = 1.6$ , 5.6, 14.0, 1H), 3.71 (td,  $J = 4.1$ , 8.2, 1H), 3.82-3.90 (several peaks, 2H), 3.94-4.02 (several peaks, 2H), 4.90 (t,  $J = 4.6$ , 1H), 5.12 (tdd,  $J = 1.3$ , 1.8, 10.4, 1H), 5.20 (qd,  $J = 1.7$ , 17.3, 1H), 5.90 (tdd,  $J = 5.8$ , 10.4, 17.3, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  29.0, 29.5, 29.7, 42.4, 62.3, 64.8 (2 peaks), 68.6, 104.3, 116.4, 135.0.

**Typical procedure for ring opening of aziridines 6:**

***N*-Allyl-erythro-2-amino-3-hydroxy-3-phenylpropyl phenyl selenide (7a):**



Aziridine **6a** (250 mg, 1.32 mmol) was dissolved in THF (10 mL) and freshly prepared benzeneselenol (280  $\mu$ L, 2.64 mmol) was added at room temp. The reaction was stirred for 1 h and diluted with  $\text{CH}_2\text{Cl}_2$ . The organic phase was extracted with  $\text{NaHCO}_3$  (5% aq.) and dried with  $\text{K}_2\text{CO}_3$ . Flash chromatography ( $\text{CH}_2\text{Cl}_2$ :MeOH = 95:5) afforded 362 mg (79%) of the title compound.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.10 (bs, 2H), 2.73 (dd,  $J$  = 9.0, 13.0, 1H), 2.78 (dd,  $J$  = 4.3, 13.0, 1H), 2.88 (ddd,  $J$  = 3.7, 4.3, 9.0, 1H), 3.26 (dddd,  $J$  = 1.2, 1.5, 6.6, 14.1, 1H), 3.36 (dddd,  $J$  = 1.4, 1.7, 5.5, 14.1, 1H), 4.94 (m, 1H), 5.09 (tdd,  $J$  = 1.2, 1.6, 10.2, 1H), 5.16 (qd,  $J$  = 1.6, 17.2, 1H), 5.84 (dddd,  $J$  = 5.6, 6.7, 10.2, 17.2, 1H), 7.17-7.23 (several peaks, 3H), 7.25-7.30 (several peaks, 5H), 7.32-7.37 (several peaks, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  27.9, 49.8, 61.2, 71.4, 116.4, 125.8, 127.0, 127.3, 128.3, 129.1, 129.4, 132.4, 136.3, 140.4.

***N*-Allyl-erythro-2-amino-3-hydroxy-3-(2-thienyl)propyl phenyl selenide (7b):** Yield 96%,

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.83-2.95 (several peaks, 3H), 3.25 (ddd,  $J$  = 1.3, 1.6, 6.1, 2H), 5.06 (tdd,  $J$  = 1.3, 1.7, 10.3, 1H), 5.12 (qd,  $J$  = 1.6, 17.2, 1H), 5.15 (dd,  $J$  = 1.0, 3.7, 1H), 5.80 (tdd,  $J$  = 6.1, 10.3, 17.3, 1H), 6.87 (ddd,  $J$  = 0.9, 1.2, 3.5, 1H), 6.97 (dd,  $J$  = 3.5, 5.1, 1H), 7.20-7.25 (several peaks, 4H), 7.38-7.42 (several peaks, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  28.3, 50.1, 61.3, 69.4, 116.5, 123.8, 124.3, 126.7, 127.1, 129.1, 129.3, 132.8, 136.1, 144.2.

***N*-Allyl-erythro-(2-amino-3-hydroxyoctyl) phenyl selenide (7c):** Yield 89%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.87 (m, 3H), 1.19-1.34 (several peaks, 6H), 1.39-1.51 (several peaks, 2H), 2.37

(bs, 2H), 2.57 (ddd,  $J = 3.2, 3.8, 9.8$ , 1H), 2.84 (dd,  $J = 9.8, 12.8$ , 1H), 3.14 (dddd,  $J = 1.2, 1.5, 6.6, 14.0$ , 1H), 3.16 (dd,  $J = 3.8, 12.8$ , 1H), 3.26 (dddd,  $J = 1.4, 1.7, 5.4, 14.0$ , 1H), 3.69 (m, 1H), 5.07 (tdd,  $J = 1.3, 1.7, 10.2$ , 1H), 5.14 (qd,  $J = 1.6, 17.2$ , 1H), 5.82 (dddd,  $J = 5.5, 6.7, 10.2, 17.2$ , 1H), 7.24-7.28 (several peaks, 3H), 7.48-7.53 (several peaks, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.0, 22.6, 26.0, 28.4, 31.9, 32.3, 49.8, 59.5, 69.6, 116.3, 127.3, 129.1, 129.2, 133.2, 136.2.

***N*-Allyl-erythro-(2-amino-3-hydroxy-4-methylpentyl) phenyl selenide (7d):** Yield 65%,

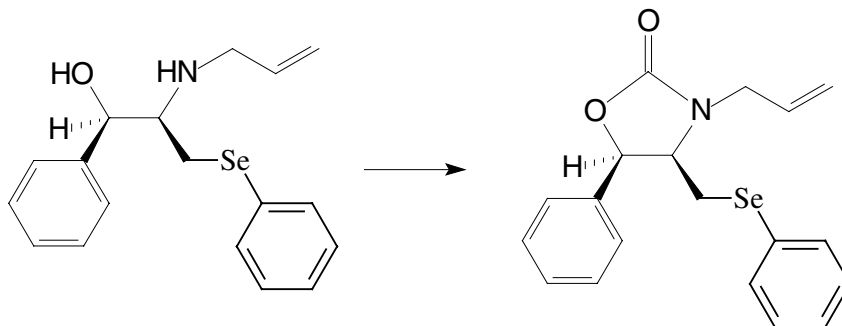
$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.66 (d,  $J = 6.7$ , 3H), 1.02 (d,  $J = 6.5$ , 3H), 1.66 (sepd,  $J = 6.6, 9.3$ , 1H), 2.64 (ddd,  $J = 2.8, 3.2, 10.6$ , 1H), 2.77 (bs, 1H), 2.79 (dd,  $J = 10.6, 12.8$ , 1H), 3.06 (dddd,  $J = 1.1, 1.4, 6.8, 14.0$ , 1H), 3.19 (dd,  $J = 2.8, 12.8$ , 1H), 3.20 (dd,  $J = 3.2, 9.3$ , 1H), 3.24 (dddd,  $J = 1.4, 1.8, 5.3, 14.0$ , 1H), 5.05 (tdd,  $J = 1.3, 1.7, 10.2$ , 1H), 5.13 (qd,  $J = 1.6, 17.2$ , 1H), 5.80 (dddd,  $J = 5.4, 6.9, 10.3, 17.1$ , 1H), 7.22-7.27 (several peaks, 3H), 7.48-7.53 (several peaks, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  17.7, 20.3, 28.4, 29.7, 49.5, 56.8, 74.7, 116.1, 127.3, 128.9 (2 peaks), 133.4, 136.2.

***N*-Allyl-erythro-[2-amino-5-(1,3-dioxolan-2-yl)-3-hydroxypentyl] phenyl selenide (7e):**

Yield 94%,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.43-1.61 (several peaks, 2H), 1.67 (dddd,  $J = 4.7, 6.0, 9.3, 13.7$ , 1H), 1.88 (bs, 2H), 1.89 (dddd,  $J = 4.4, 5.5, 9.8, 13.7$ , 1H), 2.61 (ddd,  $J = 3.5, 4.1, 9.4$ , 1H), 2.90 (dd,  $J = 9.4, 12.7$ , 1H), 3.15 (dddd,  $J = 1.2, 1.5, 6.6, 14.0$ , 1H), 3.16 (dd,  $J = 4.3, 12.7$ , 1H), 3.24 (dddd,  $J = 1.4, 1.7, 5.5, 14.0$ , 1H), 3.72 (td,  $J = 3.7, 9.2$ , 1H), 3.81-3.90 (several peaks, 2H), 3.92-4.00 (several peaks, 2H), 4.88 (dd,  $J = 4.5, 4.7$ , 1H), 5.06 (tdd,  $J = 1.3, 1.7, 10.3$ , 1H), 5.13 (qd,  $J = 1.6, 17.1$ , 1H), 5.81 (dddd,  $J = 5.6, 6.6, 10.2, 17.1$ , 1H), 7.24-7.28 (several peaks, 3H), 7.48-7.53 (several peaks, 2H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  26.6, 28.5, 30.8, 49.9, 59.7, 64.9 (2 peaks), 69.8, 104.3, 116.4, 127.3, 129.1, 129.3, 133.1, 136.2.

***N*-Allyl-(*cis*-5-phenyl-2-oxazolidinone-4-yl)methyl phenyl selenide (9):**

Selenide **7a** (130 mg, 0.37 mmol) was dissolved in dimethyl carbonate (12 mL) and NaH (60% in mineral oil, 30 mg, 0.75 mmol) was added. The mixture was stirred for 1 h and then brought to reflux. The reaction mixture was then kept refluxing until all starting material was consumed according to TLC. After dilution with diethyl ether, the organic phase was extracted with NaHCO<sub>3</sub> (5% aq.), dried with MgSO<sub>4</sub>, and evaporated. Flash chromatography (pentane:acetone = 80:20) afforded 105 mg (76%) of the title compound.

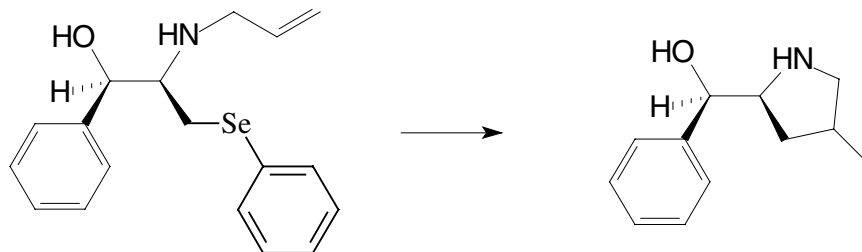
<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.55 (dd, *J* = 8.5, 13.2, 1H), 2.78 (dd, *J* = 3.7, 13.1, 1H), 3.51 (tdd, *J* = 1.1, 7.6, 15.6, 1H), 4.14 (dddd, *J* = 1.5, 1.8, 4.8, 15.7, 1H), 4.25 (ddd, *J* = 3.6, 8.1, 8.5, 1H), 5.08 (m, 1H), 5.12 (m, 1H), 5.64 (d, *J* = 8.1, 1H), 5.70 (dddd, *J* = 4.8, 7.6, 10.1, 17.1, 1H), 7.17-7.26 (several peaks, 3H), 7.33-7.38 (several peaks, 7H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 26.4, 45.2, 58.8, 78.5, 118.7, 126.8, 127.4, 128.4, 128.8, 129.0, 129.5, 131.8, 133.1, 134.0, 157.4.



**Typical procedure for radical ring-closure:**

**(2*S*\*)-2-[(1*R*\*)-1-Hydroxy-1-phenylmethyl]-4-methylpyrrolidine (**8a**):**



Selenide **7a** (100 mg, 0.29 mmol) and AIBN (7 mg, 0.04 mmol) were dissolved in dry benzene (6 mL) and argon was bubbled through the solution for five min. Freshly distilled tri-*n*-butyltin hydride (156  $\mu$ L, 0.58 mmol) was added and the solution irradiated overnight at 15  $^{\circ}$ C. The solvent was evaporated and the residue treated with HCl (10 mL 1.2 M) and pentane (10 mL). The acidic aqueous phase was extracted twice with pentane before it was made basic with either NaOH pellets or  $\text{NH}_3$  (28% aq.) (in the case of thiophene derivative **8b**,  $\text{NH}_3$  was used to minimise loss of metal-chelated material). The heterogeneous aqueous phase was then extracted with  $\text{CH}_2\text{Cl}_2$ , and the organic phase was dried with  $\text{K}_2\text{CO}_3$ . The crude product, 46 mg (82%), was almost pure (9/1 mixture of *trans* and *cis* isomers). After one recrystallization from cyclohexane, the *trans/cis*-ratio increased to > 25/1.

When the radical cyclization was performed in the presence of a Lewis acid, the protocol was slightly modified:

To argon-bubbled benzene (12 mL) were added selenide (200 mg, 0.58 mmol) and  $\text{Me}_3\text{Al}$  (320  $\mu$ L 2M solution in hexane, 0.64 mmol). The reaction mixture was stirred for 1 hour, after which AIBN (14 mg, 0.09 mmol) and tri-*n*-butyltin hydride (312  $\mu$ L, 1.16 mmol) were added. The reaction was irradiated overnight and the workup was performed as described above. In the cases where modified Lewis acids were used, 1 equivalent  $\text{Me}_3\text{Al}$  was treated with 2 equivalents of the appropriate alcohols for 1 h before the selenide was added. After another 1 h of stirring, AIBN and tri-*n*-butyltin hydride were added and irradiation started.

$^1\text{H}$  NMR *trans*-**8a** ( $\text{CDCl}_3$ )  $\delta$  0.92 (d,  $J$  = 6.8, 3H), 1.04 (ddd,  $J$  = 6.5, 8.4, 12.9, 1H), 1.84 (ddd,  $J$  = 7.0, 8.8, 12.8, 1H), 2.12 (m, 1H), 2.44 (dd,  $J$  = 7.8, 9.6, 1H), 2.94 (bs, 2H), 3.12 (dd,

$J = 6.6, 9.6, 1\text{H}$ ), 3.47 (ddd,  $J = 4.3, 7.0, 8.4, 1\text{H}$ ), 4.68 (d,  $J = 4.3, 1\text{H}$ ), 7.21-7.26 (m, 1H), 7.24-7.37 (several peaks, 4H).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.9, 33.0, 33.2, 54.9, 63.1, 74.2, 125.8, 127.0, 128.1, 142.3.

**(2*S*\*)-2-[(1*R*\*)-1-Hydroxy-1-(2-thienyl)methyl]-4-methyl pyrrolidine (8b):** Yield 80%, *trans/cis*-ratio = 9:1,  $^1\text{H}$  NMR *trans*-**8b** ( $\text{CDCl}_3$ )  $\delta$  0.95 (d,  $J = 6.7, 3\text{H}$ ), 1.27 (ddd,  $J = 6.8, 8.5, 12.8, 1\text{H}$ ), 1.93 (ddd,  $J = 6.7, 8.7, 12.9, 1\text{H}$ ), 2.12 (m, 1H), 2.44 (dd,  $J = 7.8, 9.8, 1\text{H}$ ), 3.10 (dd,  $J = 6.6, 9.8, 1\text{H}$ ), 3.32 (bs, 2H), 3.50 (ddd,  $J = 4.5, 6.5, 8.8, 1\text{H}$ ), 4.88 (d,  $J = 4.5, 1\text{H}$ ), 6.94-6.97 (several peaks, 2H), 7.21 (dd,  $J = 1.6, 4.6, 1\text{H}$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.8, 33.3, 33.9, 54.7, 63.4, 71.6, 123.4, 124.1, 126.4, 146.4.

**(2*S*\*)-2-[(1*R*\*)-1-Hydroxyhexyl]-4-methyl pyrrolidine (8c):** Yield 96%, *trans/cis*-ratio = 10:1,  $^1\text{H}$  NMR *trans*-**8c** ( $\text{CDCl}_3$ )  $\delta$  0.85 (m, 3H), 0.95 (d,  $J = 6.7, 3\text{H}$ ), 1.16-1.53 (several peaks, 9H), 1.83 (ddd,  $J = 7.2, 8.7, 12.6, 1\text{H}$ ), 2.10 (m, 1H), 2.41 (dd,  $J = 7.7, 9.7, 1\text{H}$ ), 2.74 (bs, 2H), 3.07 (dd,  $J = 6.5, 9.7, 1\text{H}$ ), 3.16 (ddd,  $J = 3.4, 7.2, 8.6, 1\text{H}$ ), 3.53 (ddd,  $J = 3.4, 4.5, 8.0, 1\text{H}$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.0, 19.0, 22.6, 25.8, 31.9, 32.3, 33.5, 33.9, 54.7, 61.6, 72.1.

**(2*S*\*)-2-[(1*R*\*)-1-Hydroxy-2-methylpropyl]-4-methyl pyrrolidine (8d):** Yield 79%, *trans/cis*-ratio = 12:1,  $^1\text{H}$  NMR *trans*-**8d** ( $\text{CDCl}_3$ )  $\delta$  0.85 (d,  $J = 6.8, 3\text{H}$ ), 0.99 (d,  $J = 6.8, 3\text{H}$ ), 1.02 (d,  $J = 6.7, 3\text{H}$ ), 1.24 (ddd,  $J = 6.3, 8.6, 12.7, 1\text{H}$ ), 1.60 (dsep,  $J = 8.6, 6.8, 1\text{H}$ ), 1.87 (ddd,  $J = 7.2, 8.7, 12.6, 1\text{H}$ ), 2.13 (m, 1H), 2.46 (dd,  $J = 7.9, 9.5, 1\text{H}$ ), 2.91 (bs, 2H), 3.12 (dd,  $J = 6.4, 9.5, 1\text{H}$ ), 3.16 (dd,  $J = 3.4, 8.5, 1\text{H}$ ), 3.38 (ddd,  $J = 3.4, 7.3, 8.5, 1\text{H}$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.6, 19.0, 19.8, 31.3, 31.8, 33.5, 54.5, 59.2, 77.4.

After sublimation of the product the *trans/cis* ratio increased to > 25/1.

**(2*S*\*)-2-[(1*R*\*)-3-(1,3-Dioxolan-2-yl)-1-hydroxypropyl]-4-methyl pyrrolidine (8e):** Yield 84%, *trans/cis*-ratio = 9:1,  $^1\text{H}$  NMR *trans*-**8e** ( $\text{CDCl}_3$ )  $\delta$  0.99 (d,  $J = 6.7, 3\text{H}$ ), 1.27 (ddd,  $J = 6.4, 8.5, 12.7, 1\text{H}$ ), 1.47-1.59 (several peaks, 2H), 1.73 (dddd,  $J = 4.8, 6.3, 9.4, 13.9, 1\text{H}$ ), 1.83-1.94 (several peaks, 2H), 2.13 (m, 1H), 2.43 (dd,  $J = 7.7, 9.9, 1\text{H}$ ), 3.10 (dd,  $J = 6.5, 9.9, 1\text{H}$ ), 3.17 (ddd,  $J = 3.9, 7.1, 8.4, 1\text{H}$ ), 3.57 (ddd,  $J = 4.0, 4.3, 8.7, 1\text{H}$ ), 3.83-3.87 (several peaks, 2H), 3.94-3.99 (several peaks, 2H), 4.89 (t,  $J = 4.7, 1\text{H}$ ).

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.9, 28.2, 30.4, 32.8, 33.4, 54.7, 61.8, 64.7 (2 peaks), 72.0, 104.5.

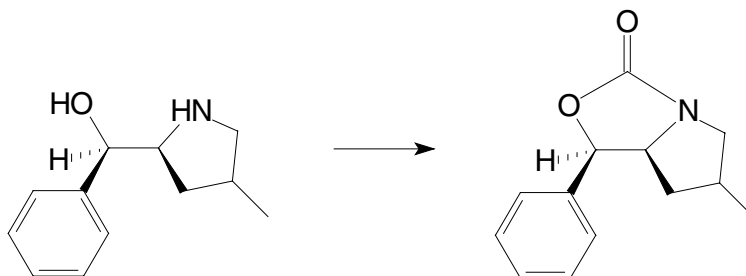
**(1*R*\*,6*R*\*,7*aS*\*)-6-Methyl-1-phenyl-tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (10):**

Yield 90%, (6*R*\*,7*aS*\*)/(6*R*\*,7*aR*\*) ratio = 6:1, <sup>1</sup>H NMR (1*R*\*,6*R*\*,7*aS*\*)-10 (CDCl<sub>3</sub>) δ 0.97 (d, 7.0, 3H), 1.08 (dddd, J = 0.5, 4.0, 6.8, 13.0, 1H), 1.33 (dddd, J = 0.4, 8.7, 9.1, 13.0, 1H), 2.23 (m, 1H), 2.27 (dd, J = 5.4, 11.7, 1H), 3.92 (tdd, J = 0.5, 7.7, 11.7, 1H), 4.32 (m, 1H), 5.81 (d, J = 8.1, 1H), 7.25-7.28 (several peaks, 2H), 7.29-7.41 (several peaks, 3H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 19.5, 32.6, 34.3, 54.2, 62.4, 77.2, 125.0, 128.2, 128.6, 135.9, 161.2.

**(1*R*\*,6*R*\*,7*aS*\*)-6-Methyl-1-phenyl-tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazol-3-one (10).**

**Alternative synthesis:**



To a solution of a diastereomeric mixture (9/1) of compound **8a** (39 mg, 0.2 mmol) in DMF (2 mL) were added NaH (60% in mineral oil, 8.2 mg, 0.4 mmol) and dimethyl carbonate (84 μL, 1 mmol). The mixture was refluxed until no starting material could be detected by TLC. The reaction mixture was then diluted with diethyl ether and washed several times with water. The organic phase was dried with MgSO<sub>4</sub> and evaporated. Flash chromatography (pentane:ether = 70:30) afforded 29.1 mg (67%) of a diastereomeric mixture (9/1) containing the title compound as the predominating product.