HETEROCYCLES, Vol. 63, No. 11, 2004, pp. 2495 - 2514
Received, 5th July, 2004, Accepted, 16th September, 2004, Published online, 17th September, 2004

# SYNTHESIS OF *N*-BRIDGEHEAD FUSED BICYCLIC β-LACTAMS THROUGH ORGANOMETAL-MEDIATED TRANSFORMATIONS OF 1,2-DIALKENYLAZIRIDINES[§]

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**Abstract** – *N*-Bridgehead fused bicyclic β-lactams have been synthesized through sequential organometal-mediated transformations of 1,2-dialkenylaziridines, namely $Co_2(CO)_8$-catalysed carbonylation and ring-closing metathesis (RCM). When firstly subjected to RCM conditions, either with Schrock-Hoveyda or Grubbs' catalyst, 1,2-dialkenylaziridines did not afford the expected bicyclic *N*-bridgehead products. In contrast, however, *cis*-1,2-dialkenylaziridines were amenable to carbonylative ring expansion, affording *trans*-1,4-dialkenyl-β-lactams which could be subsequently metathesized to the corresponding fused bicyclic compounds using Grubbs' catalyst. Unexpectedly, carbonylation of *trans*-1,2-dialkenylaziridines occurred with the unprecedented rearrangement to the 5,6-dihydro-4*H*-[1,3]oxazine skeleton.

## INTRODUCTION

Aziridines represent a valuable class of useful and highly versatile synthetic intermediates.[1] In fact, they can be prepared by several stereoselective methods[2,3] and, due to the intrinsic high strain of the aziridine ring, they are capable of undergoing sterecontrolled nucleophilic ring opening reactions, leading to a wide variety of nitrogen-containing compounds bearing the most different functionalities.[4,5] By selecting suitable substituents at the ring nitrogen or carbon atoms, aziridines can be also converted into less strained heterocycles, often in a single-step sequence. For instance, *N*-acylaziridines are known to rearrange to the corresponding oxazolines with retention of configuration,[6] whilst low-temperature rearrangement of vinyl aziridines has provided a stereoselective approach to pyrrolines,[7]

[§] This paper is dedicated to Professor *Irene Moretti* on the occasion of her retirement.

tetrahydropyridines[8] and seven-membered lactams.[9]

The relief of ring strain represents the driving force also in another ring expansion of fame, namely the $Co_2(CO)_8$-catalysed carbonylation of aziridines,[10] whereby the three-membered cycle is expanded to a β-lactam ring with insertion of carbon monoxide into the C–N bond. This reaction has proved an efficient tool for the stereoselective synthesis of substituted β-lactams[11,12] and has been also successfully applied in a formal synthesis of the carbapenem antibiotic PS-5.[13]

Despite the variety of synthetic approaches to bicyclic β-lactams,[14] to the best of our knowledge only a single example of carbonylative expansion on a 2,3-fused bicyclic aziridine has been reported in the literature so far.[10] In that case, however, the substrate that underwent carbonylation did not bear an angular nitrogen atom and led therefore to a bicyclic β-lactam fused at the 3,4 position,[10] *i.e.* the 'wrong' one if compared to β-lactam antibiotics, which normally feature a 1,4-condensation pattern instead. Hence, we were prompted to investigate whether *N*-bridgehead fused β-lactams could be prepared by carbonylation of appropriate bicyclic aziridines.

To this end, ring-closing metathesis (RCM) was envisaged as a desirable method for the formation of the second fused ring. In fact such a reaction, which occurs in the presence of either Ru- or Mo-carbene complexes as the catalyst, represents a powerful synthetic tool for the construction of nitrogen-containing heterocycles from suitable non-conjugated acyclic dienes; furthermore, RCM reactions usually proceed under mild conditions and with high functional group tolerance.[15–19] Along this line, in the past few years RCM has been successfully applied to the synthesis of a variety of bicyclic systems having the most diverse ring sizes and substitutions.[20–24] Recently, in particular, fused bicyclic β-lactams have been accessed *via* RCM, whereby formation of a second 6- to 8-membered ring onto an appropriate β-lactam scaffold acting as a conformational constraint could be attained.[20–24]

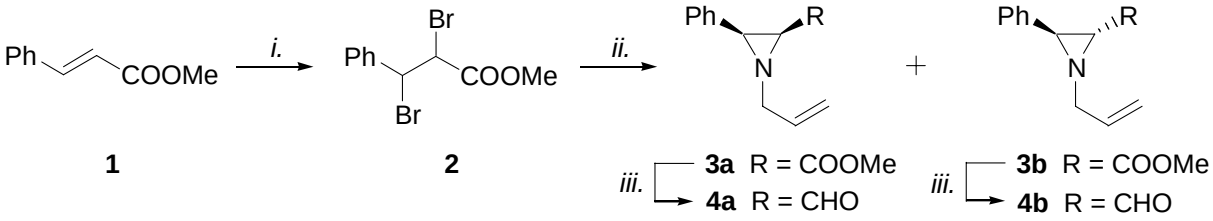
Accordingly, we reasoned that RCM onto a suitably functionalised aziridine ring could lead to a fused bicyclic system bearing the nitrogen heteroatom at the angular position, which in turn would undergo carbonylative expansion to afford the desired fused bicyclic β-lactam. To achieve this goal, two alkenyl appendages in position 1 and 2 of the aziridine ring would be required for the RCM cyclisation.

Therefore, we describe herein the synthesis of a variety of 1,2-dialkenylaziridines and their conversion into fused bicyclic β-lactams by means of sequential organometal-mediated transformations, namely RCM cyclisation and $Co_2(CO)_8$-catalysed carbonylative expansion.

## RESULTS AND DISCUSSION

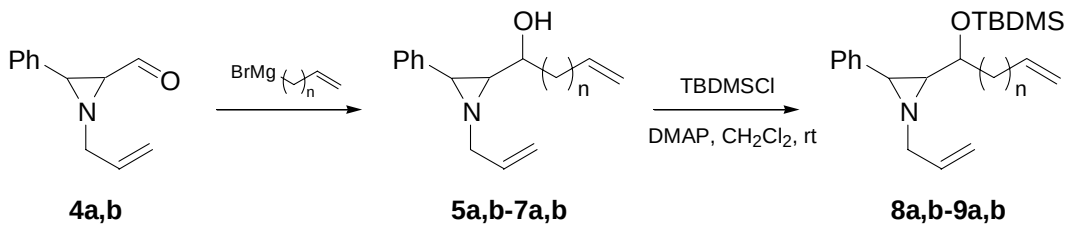
***Synthesis of 1,2-dialkenylaziridines***. – 1,2-Dialkenylaziridines were prepared by addition of an appropriate Grignard reagent to 1-allyl-2-formyl-3-phenylaziridine (**4**), which in turn was synthesized from methyl cinnamate (**1**), as outlined in Scheme 1. In particular, addition of bromine to

α,β-unsaturated ester (**1**) in *n*-hexane at reflux smoothly provided dibromo derivative (**2**), which was subjected to aminative cyclisation with allylamine in DMF at room temperature, affording *N*-allylaziridinecarboxylate (**3**) as a 55:45 mixture of *cis*/*trans* isomers (**3a** and **3b**, respectively) in 82% overall yield. The two isomers were separated by column chromatography and the ring stereochemistry was assigned on the basis of the $J_{2,3}$ constant in the $^1$H NMR spectrum.[11] Aziridines (**3a**) and (**3b**) were subsequently reduced with DIBAL-H in $CH_2Cl_2$ at –78 ºC to the corresponding formyl derivatives (**4a** and **4b**) in 79 and 70% yields, respectively.[25]




**Scheme 1.** *i*. $Br_2$, *n*-hexane, reflux (88%); *ii*. allylamine, DMF, rt (93%); *iii*. DIBAL-H, $CH_2Cl_2$, –78 ºC.

2-Formylaziridines (**4a**) and (**4b**) were alkylated with different Grignard reagents (Scheme 2) in order to introduce the second alkenyl appendage that was required for the subsequent ring-closing metathesis reaction. In the case of *cis*-aziridine (**4a**), addition of vinylmagnesium bromide in THF at –40 ºC provided derivative (**5a**) as a mixture of two diastereoisomers in a 77:23 ratio and 48% total yield (Table 1). When allylmagnesium bromide was used as the reagent, 1,2-dialkenylaziridine (**6a**) was obtained in only 26% yield, whilst 3-butenylmagnesium bromide (at –78 ºC) afforded product (**7a**) as a 62:38 mixture of diastereoisomers in 52% overall yield. As far as *trans*-aziridine (**4b**) is concerned, the same alkenylmagnesium reagents were used under similar conditions, affording the corresponding 1,2-dialkenyl derivatives (**5b-7b**), albeit in low to moderate yields (Table 1). In all cases, the two diastereoisomers could be separated by means of column chromatography; although their relative configuration could not be determined, only the first eluted diastereoisomer was selected and further processed.



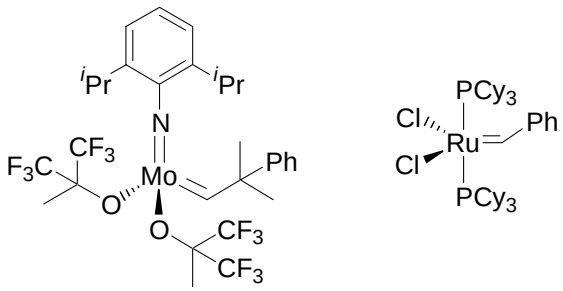

**Scheme 2.**

In addition, for aziridines (**6a,b**) and (**7a,b**) the side chain hydroxy group was protected as TBDMS ether by treatment with TBDMSCl and DMAP in methylene chloride at room temperature,[11] to afford derivatives (**8a,b**) in 60 and 34% yields, and (**9a,b**) in 39 and 75% yields, respectively (Scheme 2).

| aziridine | stereochemistry | n | solvent | product | yield (%) | diastereoisomeric ratio |
|---|---|---|---|---|---|---|
| **4a** | *cis* | 0 | THF | **5a** | 48 | 77:23 |
| **4a** | *cis* | 1 | THF | **6a** | 26 | 64:36 |
| **4a** | *cis* | 2 | THF | **7a** | 52 | 62:38 |
| **4b** | *trans* | 0 | THF | **5b** | 19 | 90:10 |
| **4b** | *trans* | 1 | $Et_2O$ | **6b** | 40 | 50:50 |
| **4b** | *trans* | 2 | $Et_2O$ | **7b** | 41 | 41:59 |

**Table 1**

***Carbonylation and ring-closing metathesis of 1,2-dialkenylaziridines.* –** Aiming to explore the feasibility of ring-closing metathesis on three-membered *N*-containing heterocycles bearing appropriate alkenyl appendages, 1,2-dialkenylaziridines (**5-6**) were subjected to RCM conditions using Schrock-Hoveyda complex (**I**) (Figure 1) as the catalyst. In fact, successful ring closures of amino dienes have been reported in the presence of **I** to yield 2,5-dihydropyrroles.[26,27] In contrast, Ru-based catalysts such as **II** (Grubbs' catalyst, Figure 1) are not effective with either secondary or tertiary amines, unless masked as amides/carbamates or ammonium salts, respectively.[28,29] On the other hand, in fact, dialkenylamides are known to metathesize successfully to *N*-containing heterocycles of various ring sizes in the presence of **II**.[15–19]

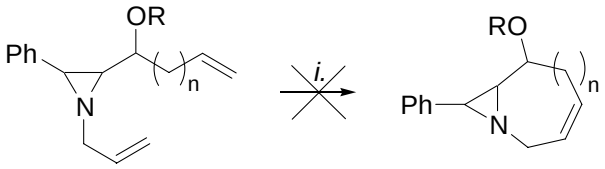



**I** **II**

**Figure 1.** – Catalysts for ring-closing metathesis (RCM)

Since any attempt to convert aziridines (**5a-7a**) into the corresponding ammonium salts met with failure, the possibility of exploiting the easy-to-use Grubbs' catalyst **II** for the formation of the second fused ring by RCM was ruled out. Therefore, we switched to Schrock-Hoveyda Mo-carbene **I** which, however, requires strictly anhydrous and oxygen-free conditions. Nonetheless, treatment of aziridines (**5-6**) with 5

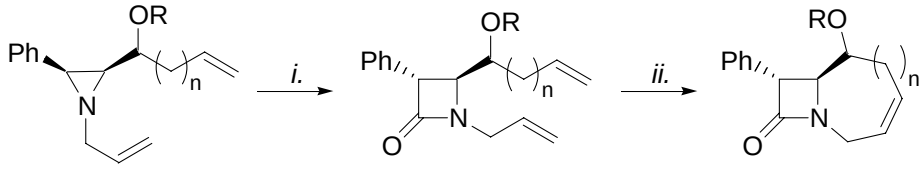
mol% **I** in either degassed $CH_2Cl_2$ or benzene at reflux did not afford the desired ring-closed product (Scheme 3) under any of the reaction conditions employed, unfortunately.




**5-6**

**Scheme 3.** *i*. Schrock-Hoveyda catalyst (**I**), $CH_2Cl_2$ or benzene, reflux.

Hence, the reaction sequence had to be reversed, and the RCM cyclisation was delayed after the carbonylative expansion of the aziridine ring (Scheme 4). *cis*-1,2-Dialkenylaziridines (**5a-9a**) were dissolved in 1,2-dimethoxyethane (DME) and treated with 500 psi carbon monoxide in the presence of $Co_2(CO)_8$ as the catalyst in 1/12 ratio at 110 ºC to afford the corresponding *trans*-1,4-dialkenyl-β-lactams (**10a-14a**) (Table 2). CO Insertion was confirmed by $^{13}C$ NMR spectroscopy, whereas the *trans* stereochemistry of the resulting β-lactam ring was assigned on the basis of the $J_{3,4}$ constant in the $^{1}H$ NMR spectrum.[11] Thereafter, β-lactams (**10a-14a**) were successfully metathesized with Grubbs' complex **II** ($CH_2Cl_2$, reflux) to the desired bicyclic compounds (**15a-19a**) in good to excellent yields (Scheme 4, Table 2).




**5a-9a** **10a-14a** **15a-19a**

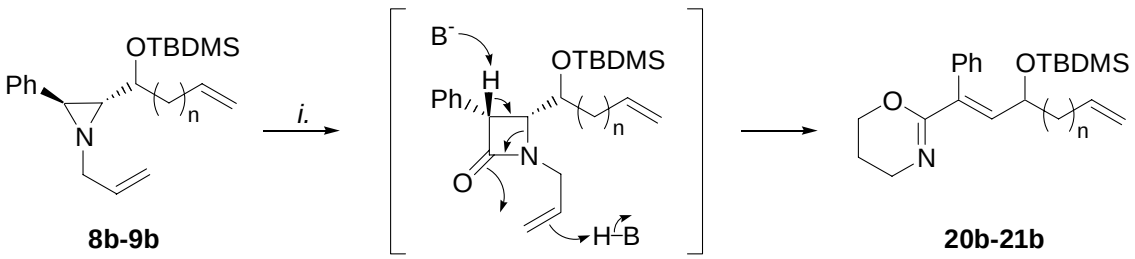
**Scheme 4.** *i*. $Co_2(CO)_8$, DME, CO (500 psi), 110 ºC; *ii*. Grubbs' catalyst (**II**), $CH_2Cl_2$, reflux.

| aziridine | n | R | monocyclic β-lactam | carbonylation yield (%) | bicyclic β-lactam | RCM yield (%) |
|---|---|---|---|---|---|---|
| **5a** | 0 | H | **10a** | 66 | **15a** | 73 |
| **6a** | 1 | H | **11a** | 42 | **16a** | 50 |
| **7a** | 2 | H | **12a** | 53 | **17a** | 88 |
| **8a** | 1 | TBDMS | **13a** | 63 | **18a** | 66 |
| **9a** | 2 | TBDMS | **14a** | 21 | **19a** | 70 |

**Table 2**

Under the same reaction conditions, *trans*-aziridines (**5b-7b**) gave rise only to a complex mixture which

was not amenable to further purification. In contrast, when *trans*-aziridines (**8b-9b**) were treated with dicobalt octacarbonyl and carbon monoxide in DME, using the same conditions reported above, disappearance of the starting material occurred and, in both cases, a new product (**20b-21b**) was isolated as a mixture of *E*/*Z* stereoisomers which could be separated by column chromatography, albeit in low overall yield (17 and 37%, respectively). MS spectroscopy confirmed the successful insertion of a CO unit, but examination of NMR spectra raised doubts as to the identity of the carbonylation products. In particular, the lack of a diagnostic doublet at 4.0–4.3 ppm accounting for the H(3) proton suggested the absence of the expected β-lactam framework and demanded for more extensive investigations by means of 2D NMR spectroscopic techniques. Accordingly, COSY experiments were performed and allowed us to assign unambiguously the 5,6-dihydro-4*H*-[1,3]oxazine structure (**20b-21b**) to the reaction products (Scheme 5). In particular, the alkenyl appendage bearing the TBDMS-protected hydroxy group was found unchanged, whilst the signals belonging to the allylic substituent at nitrogen were missing. A new spin system consisting of three $–CH_2–$ units was revealed by COSY, and one of these multiplets resonated at 3.29–3.42 ppm, suggesting the presence of a single carbon-oxygen bond, which would then force the three methylene groups within a six-membered *O*-containing azacycle, namely a 5,6-dihydro-4*H*-[1,3]oxazine.




**Scheme 5.** *i*. $Co_2(CO)_8$, DME, CO (500 psi), 110 ºC.

The unexpected formation of the 5,6-dihydro-4*H*-[1,3]oxazine skeleton would suggest that *trans* aziridines (**8b-9b**) did undergo carbonyl insertion and β-lactam formation which, however, was followed by rearrangement to products (**20b-21b**) (Scheme 5). Such a rearrangement could be explained by postulating first the formation of a *cis* β-lactam, according to a well-established mechanism.[12] Most likely, abstraction of the H(3) hydrogen, followed by cleavage of the N–C(4) bond and attack of the carbonyl oxygen to the allylic double bond would result, ultimately, in the formation of the 5,6-dihydro-4*H*-[1,3]oxazine ring, as depicted in Scheme 5.

## CONCLUSIONS

In the attempt to prepare fused bicyclic aziridines to be used for $Co_2(CO)_8$-catalysed carbonylation as an

alternative access to the *N*-bridgehead fused β-lactam motif that is normally encountered among β-lactam antibiotics, ring-closing metathesis (RCM) was tested on suitable 1,2-dialkenylaziridines. Regrettably, however, formation of a second 6- to 8-membered carbocycle onto either a *cis*- or *trans*-aziridine ring playing as a conformational constraint has proved not feasible with Schrock-Hoveyda catalyst **I**, even though no inherent functional group incompatibility in RCM with **I** was present, apparently.

In contrast, the corresponding *trans*-β-lactams, which were successfully synthesized by carbonylative ring expansion of *cis*-1,2-dialkenylaziridines, were amenable to ring-closing metathesis with Grubbs' catalyst **II**, affording *N*-bridgehead bicyclic fused systems of the [*n*.2.0] type (*n* = 4, 5, 6), in line with literature data that describe fusion of 6–8-membered carbocycles onto a β-lactam ring by means of RCM with either **I** or **II**.[20–22]

Surprisingly, carbonylation of *trans* 1,2-dialkenylaziridines in the presence of dicobalt octacarbonyl as the catalyst occurred with rearrangement to the 5,6-dihydro-4*H*-[1,3]oxazine skeleton instead, a process which is unprecedented.

## EXPERIMENTAL

$^{1}H$ and $^{13}C$ NMR were recorded in $CDCl_3$ solution on a Bruker DPX 200 MHz spectrometer; chemical shifts (δ) are reported in ppm downfield from TMS as internal standard; coupling constants (*J*) are given in Hz. For MS spectral determinations, Finnigan MAT SSQ A and Hewlett-Packard HP5972 spectrometers were used (EI, 70 eV). Elemental analyses were performed with a Carlo Erba Elemental Analyzer mod. 1110. Gas-chromatographic analyses were performed on a HP5890A gas-chromatograph equipped with a DB-1 column (J&W Scientific, 30 m length, 0.53 mm i.d., 5 μm film thickness) using helium as carrier gas. All organic solvents were dried and distilled by standard methods prior to use and all reactions requiring anhydrous conditions were performed using oven-dried and argon-flushed glassware. Chromatographic purification of compounds was carried out on silica gel (60–200 μm).

Methyl cinnamate was purchased from Aldrich. Schrock-Hoveyda (**I**) and Grubbs' (**II**) catalysts, as well as $Co_2(CO)_8$ were all from Strem Ltd. Grubbs' catalyst (**II**) was maintained in a Schlenk tube under Ar atmosphere, whilst Schrock-Hoveyda (**I**) catalyst was always handled using a dry-box under nitrogen atmosphere. $Co_2(CO)_8$ was stored in a Schlenk flask under CO atmosphere.

**Methyl 2,3-Dibromo-3-phenylpropanoate (2)** – In a 250-mL two-necked flask equipped with a reflux condenser and a dropping funnel, commercially available methyl cinnamate (**1**) (16.40 g, 101.12 mmol) was dissolved in 45 mL of *n*-hexane under gentle heating, affording a clear colorless solution. Bromine (5.7 mL, 111.23 mmol) was slowly added dropwise under magnetic stirring and the heating was gradually increased. The solution started to fade only upon reflux and, at the same time, a white solid began to crystallize. After refluxing for 30 min, the reaction mixture was cooled to rt and the precipitate

was filtered and recrystallized from *n*-hexane to afford 28.52 g of **2** as a white solid (mp 109–111 °C) in 88% yield. $^{1}$H NMR (200 MHz): δ 3.94 (3H, s, $COOCH_3$), 4.88 (1H, d, *J* 11.7, BrCHCOO), 5.38 (1H, d, *J* 11.7, C<u>H</u>BrPh), 7.34–7.47 (5H, m, arom). MS, *m/z*: 324-322-320 (Br pattern, $M^+$, 4%), 293-291-289 (2), 265-263-261 (3), 243-241 (58), 184-182 (8), 171-169 (6), 161 (16), 131 (52), 121 (86), 103 (100), 77 (55), 59 (37). Anal. Calcd for $C_{10}H_{10}O_2Br_2$: C, 37.30; H, 3.13. Found C, 37.57; H, 3.44.

***cis*- and *trans*-1-Allyl-2-methoxycarbonyl-3-phenylaziridine (3a** and **3b) –** Dibromo derivative (**2**) (10.5 g, 32.6 mmol) was dissolved in 40 mL of anhydrous DMF in a 250-mL two-necked flask equipped with a reflux condenser and a dropping funnel, and cooled to 0–5 °C with a water–ice bath. A solution of allylamine (8.56 mL, 114.1 mmol) in 10 mL of dry DMF was added dropwise and the mixture was stirred for 24 h at rt. The orange solution was poured in 600 mL of water and extracted with light petroleum (6 × 150 mL). The organic phases were combined, dried over $MgSO_4$, filtered and rotary evaporated, to provide a yellow residue. Purification by column chromatography (light petroleum/ether 70:30) afforded aziridines *trans* **3b** (2.96 g) and *cis* **3a** (3.61 g) as yellow oils in a total 93% yield.

**3a:** $^{1}$H NMR (200 MHz): δ 2.54 (1H, d, *J* 6.9, CHCOO), 2.93 (1H, d, *J* 6.9, PhC<u>H</u>), 3.04 (1H, ddt, *J* 14.1, 5.7, 1.3, $NCH_2$), 3.30 (1H, dd, *J* 14.1, 5.4, $NCH_2$), 3.44 (3H, s, $COOCH_3$), 5.13 (1H, dq, *J* 10.4, 1.3, CH=C<u>H</u>$_2$), 5.28 (1H, dq, *J* 17.2, 1.7, CH=C<u>H</u>$_2$), 5.85–6.10 (1H, m, C<u>H</u>=$CH_2$), 7.14–7.43 (5H, m, arom). $^{13}$C NMR: δ 178.8, 135.3, 134.4, 128.3, 128.0, 127.8, 117.8, 62.9, 52.0, 48.1, 46.2. MS, *m/z*: 217 ($M^+$, 4%), 216 (13), 188 (1), 187 (2), 186 (9), 177 (5), 176 (62), 161 (3), 159 (2), 158 (19), 144 (16), 131 (12), 121 (12), 116 (100), 103 (7), 91 (20), 89 (25), 77 (18).[30] Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found C, 71.74; H, 6.71; N, 6.28.

**3b:** $^{1}$H NMR (200 MHz): δ 2.80 (1H, d, *J* 2.7, CHCOO), 3.22 (1H, br s, PhC<u>H</u>), 3.60 (1H, br s, $NCH_2$), 3.70 (1H, br s, $NCH_2$), 3.78 (3H, s, $COOCH_3$), 5.12 (1H, d, *J* 10.4, CH=C<u>H</u>$_2$), 5.26 (1H, d, *J* 17.1, CH=C<u>H</u>$_2$), 5.91–6.08 (1H, m, C<u>H</u>=$CH_2$), 7.24–7.38 (5H, m, arom). $^{13}$C NMR: δ 169.1, 135.2, 133.9, 128.4, 127.9, 127.7, 127.5, 126.3, 117.5, 116.4, 62.5, 53.8, 52.1, 51.7, 48.1, 47.7, 45.7, 44.1. MS, *m/z*: 217 ($M^+$, 4%), 216 (13), 188 (1), 187 (2), 186 (9), 177 (5), 176 (62), 161 (3), 159 (2), 158 (19), 144 (16), 131 (12), 121 (12), 116 (100), 103 (7), 91 (20), 89 (25), 77 (18).[30] Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found C, 72.02; H, 7.15; N, 6.28.

***cis*-1-Allyl-2-formyl-3-phenylaziridine (4a) –** Aziridine (**3a**) (2.00 g, 9.21 mmol) was dissolved in 22 mL of anhydrous dichloromethane in a 250-mL three-necked flask equipped with a reflux condenser and a dropping funnel and cooled at –78 °C. A 1.2 M solution of DIBAL-H in toluene (11.5 mL, 13.8 mmol) was then added under mechanical stirring and Ar atmosphere during a 30 min period; particular care was taken in cooling the DIBAL-H solution before addition by letting it flow dropwise along the cold flask surface before it came into contact with the reaction mixture. After 1 h, sodium fluoride (7.0 g, 167

mmol) was added under vigorous stirring, followed by water (4.8 mL). The solution became turbid and a white precipitate formed. The cold bath was then removed and the mixture was allowed to warm to rt. Ether (200 mL) was added and the light yellow gelatinous solid which precipitated was filtered off, washing with abundant ether. The clear solution was dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a crude residue that was chromatographed on silica gel (ether/light petroleum 70:30), affording formylaziridine (**4a**) as a pale yellow oil (1.352 g, 79%) $^1$H NMR (200 MHz): δ 2.35 (1H, t, *J* 6.6, C<u>H</u>CHO), 3.10 (1H, d, *J* 6.7, PhC<u>H</u>), 3.17 (1H, ddt, *J* 14.1, 5.7, 1.5, $NCH_2$), 3.29 (1H, ddt, *J* 14.1, 5.7, 1.5, $NCH_2$), 5.15–5.38 (2H, m, CH=C<u>H</u>$_2$), 5.88–6.14 (1H, m, C<u>H</u>=$CH_2$), 7.10–7.60 (5H, m, arom), 8.98 (1H, d, *J* 6.6, CHO). $^{13}$C NMR: δ 202.2, 136.4, 128.7, 128.5, 128.2, 118.0, 71.6, 51.5, 46.4 (quaternary C not seen). MS, *m/z*: 186 ([M–1]$^+$, 12%), 185 (77), 184 (14), 168 (10), 167 (12), 156 (11), 128 (6), 127 (3), 107 (4), 91 (100), 77 (7), 65 (32), 51 (16). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found C, 77.13; H, 6.86; N, 7.56.

***trans*-1-Allyl-2-formyl-3-phenylaziridine (4b) –** By close analogy to the preparation of **4a**, *trans*-aziridinecarboxylate (**3b**) (504 mg, 2.32 mmol) dissolved in 6 mL of dry $CH_2Cl_2$ was reduced with 1.2 M DIBAL-H in toluene (4.1 mL, 4.87 mmol) at –78 °C. Similar workup as above, followed by chromatography with the same eluant, afforded **4b** as a yellow liquid (300 mg, 70%). $^1$H NMR spectroscopy showed broad and poorly resolved signals, indicating the presence of two invertomers at nitrogen. $^1$H NMR (200 MHz): δ 2.83 (1H, br s, C<u>H</u>CHO), 3.15–4.00 (3H, br m, PhC<u>H</u> and $NCH_2$), 4.90–5.40 (2H, br m, CH=C<u>H</u>$_2$), 5.75–6.10 (1H, br m, C<u>H</u>=$CH_2$), 7.15–7.45 (5H, m, arom), 9.68 (1H, br s, CHO). $^{13}$C NMR: δ 198.4, 136.0, 129.9, 129.4, 127.6, 118.3, 56.2, 52.5, 51.2 (quaternary C not seen). MS, *m/z*: 188 ([M+1]$^+$, 2%), 184 (100), 167 (19), 155 (11), 128 (7), 107 (4), 91 (67). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found C, 77.28; H, 7.18; N, 7.31.

**Alkylation of formylaziridines (4a-4b). Typical procedure. –** The formyl aziridine (2.36 mmol) was dissolved in 20 mL of dry ether or THF in a 50-mL two-necked flask equipped with a reflux condenser and a bubbler. The flask was cooled (see below under entries **5a,b-7a,b** for the appropriate value) and the appropriate Grignard reagent (1.0 M in ether or THF) was slowly added dropwise under Ar flow and magnetic stirring. The mixture became turbid, and a pale yellow solid precipitated. After 40 min the cold bath was replaced with ice and the reaction mixture was stirred for additional 50 min. When the flask was removed from the ice bath, precipitation of a conspicuous yellow solid was observed. The mixture was then diluted with ether (100 mL), poured in water (80 mL) and the aqueous phase was adjusted to pH 9 with $NH_4Cl$. After separation of the organic layer, the aqueous phase was extracted with ether (3 × 60 mL). The organic layers were pooled, washed with brine (60 mL), dried ($MgSO_4$) and evaporated *in vacuo* to give a crude residue which was purified by silica gel chromatography using the solvents

reported below.

***cis*-1-Allyl-2-(1-hydroxy-2-propenyl)-3-phenylaziridine (5a) –** Alkylation of **4a** with vinylmagnesium bromide in THF at –40 °C, followed by work-up as above afforded the title compound (**5a**) in 48% yield as a 77/23 mixture of two diastereoisomers which were separated by column chromatography using $Et_2O$/light petroleum 30:70 as the eluant.

*1st eluted*: orange oil; $^1$H NMR (200 MHz): δ 1.56 (1H, br s, OH), 1.87 (1H, dd, *J* 8.4, 6.4, PhCHC<u>H</u>), 2.78 (1H, d, *J* 6.4, PhC<u>H</u>), 3.07 (1H, ddt, *J* 13.8, 5.9, 1.4, $NCH_2$), 3.26 (1H, ddt, *J* 13.8, 5.9, 1.4, $NCH_2$), 3.66 (1H, t, *J* 6.7, C<u>H</u>OH), 5.12–5.39 (2H, m, CH=C<u>H</u>$_2$), 5.89–6.14 (2 × 1H, m, C<u>H</u>=$CH_2$), 7.22–7.49 (5H, m, arom). $^{13}$C NMR: δ 139.1, 137.2, 135.4, 128.6, 128.1, 127.4, 117.2, 115.3, 70.5, 63.3, 50.8, 46.0. MS, *m/z*: 215 ([M]$^+$, 3%), 214 (14), 198 (19), 186 (10), 175 (7), 174 (59), 158 (28), 146 (44), 144 (21), 129 (36), 118 (74), 117 (78), 104 (22), 99 (24), 98 (26), 91 (100), 77 (17), 68 (21), 55 (6).[30] Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found C, 78.26; H, 8.06; N, 6.41.

*2nd eluted*: yellowish oil; $^1$H NMR (200 MHz): δ 1.92 (1H, dd, *J* 8.3, 6.7, PhCHC<u>H</u>), 2.83 (1H, d, *J* 6.7, PhC<u>H</u>), 2.68 (1H, br s, OH), 3.08 (1H, dd, *J* 13.8, 6.0, $NCH_2$), 3.31 (1H, dd, *J* 13.8, 5.8, $NCH_2$), 3.59 (1H, ddt, *J* 8.3, 5.3, 1.4, C<u>H</u>OH), 4.97–5.39 (2 × 2H, m, CH=C<u>H</u>$_2$), 5.63–5.83 (1H, m, C<u>H</u>=$CH_2$), 5.94–6.17 (1H, m, C<u>H</u>=$CH_2$), 7.18–7.47 (5H, m, arom). $^{13}$C NMR: δ 137.6, 135.3, 128.5, 127.9, 127.4, 117.6, 115.6, 70.8, 63.5, 51.2, 46.7 (quaternary C not seen). MS, *m/z*: 215 ([M]$^+$, 3%), 214 (14), 198 (19), 186 (10), 175 (7), 174 (59), 158 (28), 146 (44), 144 (21), 129 (36), 118 (74), 117 (78), 104 (22), 99 (24), 98 (26), 91 (100), 77 (17), 68 (21), 55 (6).[30] Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found C, 77.95; H, 8.15; N, 6.29.

***trans*-1-Allyl-2-(1-hydroxy-2-propenyl)-3-phenylaziridine (5b) –** Alkylation of aziridine (**4b**) with vinyl magnesium bromide in THF at –40 °C afforded **5b** in 19% yield as a 90:10 mixture of diastereoisomers, which were purified by column chromatography (ether/light petroleum 70:30). $^1$H NMR spectroscopy showed broad and poorly resolved signals, indicating the presence of two invertomers at nitrogen. Due to the paucity of material, the slow-eluting isomer could not be characterized in full.

*1st eluted*: orange oil; $^1$H NMR (200 MHz): δ 2.20–2.40 (1H, br m, PhCHC<u>H</u>); 2.55–2.75 (1H, br m, $NCH_2$); 2.80–3.05 (1H, br m, $NCH_2$); 3.28–3.33 (1H, br, PhC<u>H</u>); 3.50 (1H, br, OH); 4.25–4.40 (1H, br m, C<u>H</u>OH); 4.80–5.50 (4H, br m, 2 × CH=C<u>H</u>$_2$); 5.65–6.15 (2H, br m, 2 × C<u>H</u>=$CH_2$); 7.00–7.65 (5H, m, arom). $^{13}$C NMR: δ 137.0, 131.2, 130.6, 129.2, 128.5, 125.9, 116.8, 116.5, 70.2, 65.9, 30.7, 30.0. MS, *m/z*: 215 ([M+1]$^+$), 198, 186, 174, 170, 158, 146, 129, 117, 91 (base peak), 77, 68, 63, 55.[30] Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found C, 78.34; H, 7.81; N, 6.66.

***cis*-1-Allyl-2-(1-hydroxy-3-butenyl)-3-phenylaziridine (6a) –** By close analogy to the preparation of **5a**, aziridine (**4a**) was alkylated with allylmagnesium bromide in diethyl ether at –20 °C. After work-up and chromatography (ether/light petroleum 80:20), the two diastereoisomers were isolated in 26% overall yield in 64:36 ratio.

*1st eluted*: orange thick oil; $^1$H NMR (200 MHz): δ 1.77 (1H, dd, *J* 8.0, 6.7, PhCHC<u>H</u>), 1.90–2.20 (2H, m, CHOHC<u>H</u>$_2$), 2.45 (1H, br s, OH), 2.66 (1H, d, *J* 6.7, PhC<u>H</u>), 2.96 (1H, ddt, *J* 14.0, 5.9, 1.4, NCH$_2$), 2.99–3.08 (1H, m, C<u>H</u>OH), 3.17 (1H, ddt, *J* 13.8, 5.7, 1.4, NCH$_2$), 4.80–4.95 (2H, m, CH=C<u>H</u>$_2$), 5.05 (1H, dq, *J* 10.3, 1.3, CH=C<u>H</u>$_2$), 5.18 (1H, dq, *J* 17.2, 1.6, CH=C<u>H</u>$_2$), 5.54 (1H, ddt, *J* 16.5, 9.5, 6.5, NCH$_2$C<u>H</u>=), 5.92 (1H, ddt, *J* 17.2, 10.3, 5.9, CHOHCH$_2$C<u>H</u>=), 7.09–7.34 (5H, m, arom). $^{13}$C NMR: δ 138.1, 136.3, 135.5, 129.5, 128.8, 128.3, 118.6, 118.5, 69.7, 64.6, 52.3, 48.0, 40.5. MS, *m/z*: 229 ([M+1]$^+$, 2%), 228 (13), 212 (10), 188 (26), 158 (22), 118 (35), 91 (100), 77 (20), 55 (6). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found C, 78.78; H, 8.29; N, 6.19.

*2nd eluted*: orange oil; $^1$H NMR (200 MHz): δ 1.85 (1H, dd, *J* 8.5, 6.4, NC<u>H</u>Ph); 1.95–2.15 (2H, m, CHOHC<u>H</u>$_2$); 2.50 (1H, br, OH); 2.72 (1H, d, *J* 6.4, PhC<u>H</u>); 3.04 (1H, ddt, *J* 13.9, 5.6, 1.5, NCH$_2$); 3.19 (1H, ddt, *J* 13.9, 6.1, 1.4, NCH$_2$); 3.26–3.32 (1H, m, C<u>H</u>OH); 4.98–5.09 (2H, m, CH=C<u>H</u>$_2$); 5.12 (1H, dq, *J* 10.1, 1.6, CH=C<u>H</u>$_2$); 5.22 (1H, dq, *J* 17.6, 1.6, CH=C<u>H</u>$_2$); 5.79 (1H, ddt, *J* 16.6, 10.4, 7.0, NCH$_2$C<u>H</u>=); 5.96 (1H, ddt, *J* 17.6, 10.1, 6.3, CHCH$_2$C<u>H</u>=); 7.15–7.48 (5H, m, arom). $^{13}$C NMR: δ 139.2, 136.8, 134.9, 128.3, 127.4, 127.0, 117.0, 116.3, 66.8, 63.0, 50.7, 45.8, 37.6. MS, *m/z*: 229 ([M+1]$^+$, 2%), 228 (13), 212 (10), 188 (26), 158 (22), 118 (35), 91 (100), 77 (20), 55 (6). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found C, 78.83; H, 8.18; N, 6.28.

***trans*-1-Allyl-2-(1-hydroxy-3-butenyl)-3-phenylaziridine (6b) –** Similarly as above, alkylation of **4b** with allylmagnesium bromide gave the title compound in 40% total yield as a mixture of separable diastereoisomers (ether/light petroleum 80:20) in 50:50 ratio.

*1st eluted*: yellow oil; $^1$H NMR (200 MHz): δ 2.26 (1H, t, *J* 3.6, PhCHC<u>H</u>), 2.40 (2H, t, *J* 5.5, CHOHC<u>H</u>$_2$), 2.61 (1H, dd, *J* 14.3, 5.9, NCH$_2$), 2.93 (2H, *J* 14.3, 5.0, OH and NCH$_2$), 3.34 (1H, d, *J* 3.5, PhC<u>H</u>), 3.93 (1H, dt, *J* 3.8, 6.3, C<u>H</u>OH), 4.95–5.26 (2 × 2H, m, CH=C<u>H</u>$_2$), 5.68–6.10 (2 × 1H, m, C<u>H</u>=CH$_2$), 7.15–7.45 (5H, m, arom). $^{13}$C NMR: δ 136.8, 135.7, 131.8, 129.5, 129.3, 119.0, 117.5, 69.5, 55.2, 47.1, 43.5, 40.8 (quaternary C not seen). MS, *m/z*: 229 ([M+1]$^+$, 3%), 228 (9), 212 (8), 188 (35), 158 (18), 118 (39), 91 (100), 77 (25), 55 (10). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found C, 78.67; H, 8.43; N, 6.30.

*2nd eluted*: yellow oil; $^1$H NMR (200 MHz): δ 2.24 (1H, dd, *J* 6.0, 3.6, PhCHC<u>H</u>), 2.44 (2H, t, *J* 6.7, CHOHC<u>H</u>$_2$), 2.64 (1H, dd, *J* 14.0, 6.3, NCH$_2$), 2.86 (1H, dd, *J* 14.0, 5.5, NCH$_2$), 3.09 (1H, br s, OH), 3.26 (1H, d, *J* 3.3, PhC<u>H</u>), 3.59 (1H, q, *J* 5.5, C<u>H</u>OH), 4.96–5.21 (2 × 2H, m, CH=C<u>H</u>$_2$), 5.68-6.10 (2 × 1H, m, C<u>H</u>=CH$_2$), 7.14–7.50 (5H, m, arom). $^{13}$C NMR: δ 136.9, 135.7, 131.7, 129.5, 129.3, 118.9, 118.1,

72.1, 55.7, 45.8, 41.8, 31.7 (quaternary C not seen). MS, *m/z*: 229 ($[M+1]^+$, 3%), 228 (9), 212 (8), 188 (35), 158 (18), 118 (39), 91 (100), 77 (25), 55 (10). Anal. Calcd for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found C, 78.71 H, 8.60; N, 6.36.

***cis*-1-Allyl-2-(1-hydroxy-4-pentenyl)-3-phenylaziridine (7a) –** Alkylation of aziridine (**4a**) with but-3-enylmagnesium bromide (prepared from commercially available 4-bromo-1-butene) in ether at –78 °C, followed by usual work-up provided the title aziridine (**7a**) in 52% overall yield as a mixture of two diastereoisomers in 62:38 ratio, which were amenable to separation by chromatography (ether/light petroleum 70:30).

*1st eluted*: yellow oil; $^1$H NMR (200 MHz): δ 1.55–1.80 (2H, m, $CH_2C\underline{H}_2CH=CH_2$), 1.81 (1H, dd, *J* 8.3, 6.5, PhCHC<u>H</u>), 1.98–2.36 (2H, m, CHOHC$\underline{H}_2$), 2.71 (1H, d, *J* 6.5, PhC<u>H</u>), 3.04 (1H, dd, *J* 13.8, 5.8, $NCH_2$), 3.17 (1H, dt, *J* 4.1, 8.3, C<u>H</u>OH), 3.22 (1H, dd, *J* 13.8, 6.0, $NCH_2$), 4.90–5.35 (4H, m, CH=C$\underline{H}_2$), 5.73–6.10 (2H, m, C<u>H</u>=$CH_2$), 7.17–7.50 (5H, m, arom). $^{13}$C NMR: δ 138.5, 137.0, 135.0, 128.3, 127.5, 126.9, 116.9, 114.6, 69.1, 63.1, 50.9, 45.5, 34.7, 29.7. MS, *m/z*: 243 ($[M+1]^+$, 2%), 242 (14), 226 (13), 202 (27), 158 (19), 118 (30), 91 (100), 77 (23), 55 (7). Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found C, 79.11; H, 8.79; N, 5.62.

*2nd eluted*: yellow oil; $^1$H NMR (200 MHz): δ 1.33–1.65 (2H, m, $CH_2C\underline{H}_2CH=CH_2$), 1.84 (1H, dd, *J* 8.1, 6.7, PhCHC<u>H</u>), 1.90–2.02 (2H, m, CHOHC$\underline{H}_2$), 2.67 (1H, br s, O<u>H</u>), 2.76 (1H, d, *J* 6.7, PhC<u>H</u>), 2.98–3.10 (2H, m, $NCH_2$ and C<u>H</u>OH), 3.29 (1H, dd, *J* 13.8, 5.7, $NCH_2$), 4.74-5.40 (4H, m, CH=C$\underline{H}_2$), 5.56 (1H, ddt, *J* 16.7, 10.3, 6.5, C<u>H</u>=$CH_2$), 6.15 (1H, ddt, *J* 17.2, 10.3, 5.8, C<u>H</u>=$CH_2$), 7.10–7.52 (5H, m, arom). $^{13}$C NMR: δ 138.1, 136.8, 135.0, 128.1, 127.4, 126.9, 117.1, 114.4, 68.3, 63.3, 51.7, 46.7, 33.7, 29.1. MS, *m/z*: 243 ($[M+1]^+$, 2%), 242 (14), 226 (13), 202 (27), 158 (19), 118 (30), 91 (100), 77 (23), 55 (7). Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found C, 79.25; H, 8.83; N, 5.55.

***trans*-1-Allyl-2-(1-hydroxy-4-pentenyl)-3-phenylaziridine (7b) –** *trans*-Aziridine (**7b**) was prepared by close analogy to the procedure described above. Chromatography with ether/light petroleum 80:20 as the eluant afforded the two diastereoisomers in 41:59 ratio in 41% yield. For the slow-eluting diastereoisomer, $^1$H NMR spectroscopy showed the presence of two invertomers at nitrogen, due to slow nitrogen inversion on the NMR scale.

*1st eluted*: yellowish oil; $^1$H NMR (200 MHz): δ 1.69 (2H, q, *J* 7.1, $CH_2$), 2.12–2.45 (3H, m, $CH_2$ and PhCHC<u>H</u>), 2.61 (1H, dd, *J* 14.4, 5.9, $NCH_2$), 2.92 (1H, dd, *J* 14.4, 5.1, $NCH_2$), 3.22 (1H, br s, -OH), 3.32 (1H, d, *J* 3.5, PhC<u>H</u>), 3.88 (1H, dt, *J* 3.9, 6.2, C<u>H</u>OH), 4.94–5.14 (4H, m, CH=C$\underline{H}_2$), 5.70–5.99 (2H, m, C<u>H</u>=$CH_2$), 7.20–7.45 (5H, m, arom). $^{13}$C NMR: δ 138.4, 135.5, 133.5, 130.3, 128.2, 127.9, 116.0, 114.7, 68.0, 53.9, 46.3, 41.9, 34.0, 29.7. MS, *m/z*: 243 ($[M+1]^+$, 4%), 242 (11), 226 (10), 202 (31), 158 (14), 118 (41), 91 (100), 77 (22), 55 (8). Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found C, 78.79; H, 8.59; N, 5.84.

*2nd eluted*: yellowish oil; $^1$H NMR (200 MHz): δ 1.59–1.89 (2H, m, $CH_2$), 2.09–2.45 (4H, m, $CH_2$, PhCHC<u>H</u> and O<u>H</u>), 2.69 (1H, dd, *J* 14.1, 6.2, $NCH_2$), 2.86 (1H, dd, *J* 14.1, 5.6, $NCH_2$), 3.25 (1H, d, *J* 3.5, PhC<u>H</u>), 3.40–3.70 (1H, m, C<u>H</u>OH), 4.92–5.21 (4H, m, CH=C<u>H</u>$_2$), 5.71–6.97 (2H, m, C<u>H</u>=$CH_2$), 7.20–7.51 (5H, m, arom). $^{13}$C NMR: δ 138.3, 135.4, 130.3, 128.1, 128.0, 127.0, 116.7, 114.8, 71.1, 54.4, 47.6, 44.7, 34.8, 29.8. MS, *m/z*: 243 ([M+1]$^+$, 4%), 242 (11), 226 (10), 202 (31), 158 (14), 118 (41), 91 (100), 77 (22), 55 (8). Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found C, 79.21; H, 8.85; N, 5.89.

**Protection of aziridines (6,7a-b). General procedure. –** The aziridine (0.5 mmol) was dissolved in 2 mL anhydrous dichloromethane and DMAP (79 mg, 0.65 mmol) and TBDMSCl (90 mg, 0.6 mmol) were added at rt under magnetic stirring. When TLC showed disappearance of the starting material, the reaction mixture was diluted with 13 mL of $CH_2Cl_2$, washed with water (5 mL), dried and concentrated *in vacuo*. Final purification was achieved by means of column chromatography, using the eluant indicated below [in square brackets].

***cis*-1-Allyl-2-(1-*tert*-butyldimethylsilyloxy-3-butenyl)-3-phenylaziridine (8a) –** After chromatography [light petroleum/ether 90:10], the title compound was obtained as an oil in 60% yield. $^1$H NMR (200 MHz): δ 0.08 (3H, s, $^t$Bu<u>Me</u>$_2$Si), 0.21 (3H, s, $^t$Bu<u>Me</u>$_2$Si), 0.97 (9H, s, $^t$<u>Bu</u>Me$_2$Si), 1.86 (1H, dd, *J* 8.8, 6.7, PhCHC<u>H</u>), 1.93–2.05 (2H, m, SiOCHC<u>H</u>$_2$), 2.59 (1H, d, *J* 6.7, PhC<u>H</u>), 2.72 (1H, ddt, *J* 14.1, 6.2, 1.4, $NCH_2$), 3.19 (1H, dt, *J* 8.8, 5.5, CHOSi), 3.57 (1H, ddt, *J* 14.1, 5.2, 1.5, $NCH_2$), 4.81–4.98 (2H, m, CH=C<u>H</u>$_2$), 5.10 (1H, dq, *J* 10.5, 2.1, CH=C<u>H</u>$_2$), 5.26 (1H, dq, *J* 17.2, 2.1, CH=C<u>H</u>$_2$), 5.65 (1H, ddt, *J* 16.9, 10.3, 7.1, C<u>H</u>=$CH_2$), 6.01 (1H, dddd, *J* 17.2, 10.5, 6.1, 5.2, C<u>H</u>=$CH_2$), 7.19–7.45 (5H, m, arom). $^{13}$C NMR: δ 137.8, 135.6, 134.8, 127.9, 127.5, 126.6, 116.6, 116.1, 71.3, 63.3, 51.3, 45.5, 40.0, 26.0, 18.2, –4.0, –4.6. MS, *m/z*: 343 ([M]$^+$, 11%), 302 (72), 286 (66), 216 (29), 204 (48), 185 (23), 175 (25), 131 (50), 115 (13), 73 (100). Anal. Calcd for $C_{21}H_{33}NOSi$: C, 73.41; H, 9.68; N, 4.08. Found C, 73.54; H, 9.79; N, 4.21.

***trans*-1-Allyl-2-(1-*tert*-butyldimethylsilyloxy-3-butenyl)-3-phenylaziridine (8b) –** Chromatography [light petroleum/diethyl ether 70:30] afforded the desired product (**8b**) as a yellow oil, albeit in low yield (34%). $^1$H NMR spectroscopy showed broad and poorly resolved signals, indicating the presence of two invertomers at nitrogen. $^1$H NMR (200 MHz): δ 0.13 (3H, br s, $^t$Bu<u>Me</u>$_2$Si), 0.16 (3H, s, $^t$Bu<u>Me</u>$_2$Si), 0.96 (9H, s, $^t$<u>Bu</u>Me$_2$Si), 2.21 (1H, dd, *J* 7.2, 3.7, PhCHC<u>H</u>), 2.30–2.58 (2H, m, SiOCHC<u>H</u>$_2$), 2.60–2.90 (2H, br m, $NCH_2$), 3.11 (1H, d, *J* 3.7, PhC<u>H</u>), 3.51 (1H, br q, *J* 6.2, CHOSi), 4.88–5.27 (4H, m, CH=C<u>H</u>$_2$), 5.67–6.08 (2H, m, C<u>H</u>=$CH_2$), 7.05–7.36 (5H, m, arom). $^{13}$C NMR: δ 137.5, 135.9, 131.8, 128.4, 129.1, 118.6, 117.5, 76.5, 56.3, 48.4, 45.9, 42.2, 27.3, 19.5, –2.8, –3.2. MS, *m/z*: 343 ([M]$^+$, 11%), 302 (72), 286

(66), 216 (29), 204 (48), 185 (23), 175 (25), 131 (50), 115 (13), 73 (100). Anal. Calcd for $C_{21}H_{33}NOSi$: C, 73.41; H, 9.68; N, 4.08. Found C, 73.49; H, 9.73; N, 4.25.

***cis*-1-Allyl-2-(1-*tert*-butyldimethylsilyloxy-4-pentenyl)-3-phenylaziridine (9a) –** Purification by column chromatography using the same eluant as above provided the title compound as a yellow oil in 39% yield. $^1$H NMR (200 MHz): δ –0.41 (6H, s, $^t$BuMe$_2$Si), 0.79 (9H, s, $^t$BuMe$_2$Si), 1.68–1.84 (2H, m, $CH_2$), 1.85 (1H, dd, *J* 8.1, 6.3, PhCHCH), 2.09–2.29 (2H, m, $CH_2$), 2.63 (1H, d, *J* 6.3, PhCH), 2.99 (1H, ddt, *J* 14.1, 5.6, 1.3, $NCH_2$), 3.22-3.31 (2H, m, $NCH_2$ and CHOSi), 4.90–5.30 (4H, m, CH=C$H_2$), 5.75–6.08 (2H, m, CH=$CH_2$), 7.22–7.32 (5H, m, arom). $^{13}$C NMR: δ 140.4, 138.2, 136.6, 129.3, 129.2, 128.1, 118.0, 115.6, 68.7, 64.9, 53.3, 47.9, 36.9, 30.3, 27.2, 19.3, –3.5, –3.9. MS, *m/z*: 357 ([M]$^+$, 9%), 342 (2), 316 (13), 300 (32), 226 (6), 216 (20), 198 (64), 184 (44), 175 (16), 144 (17), 115 (16), 106 (20), 104 (20), 91 (25). Anal. Calcd for $C_{22}H_{35}NOSi$: C, 73.89; H, 9.87; N, 3.92. Found C, 74.04; H, 9.91; N, 3.86.

***trans*-1-Allyl-2-(1-*tert*-butyldimethylsilyloxy-4-pentenyl)-3-phenylaziridine (9b) –** After chromatography [light petroleum/ether 50:50] the title compound was isolated as a yellow oil in 75% yield. $^1$H NMR (200 MHz): δ 0.00 (3H, s, $^t$BuMe$_2$Si), 0.06 (3H, s, $^t$BuMe$_2$Si), 0.89 (9H, s, $^t$BuMe$_2$Si), 1.63–1.95 (2H, m, $CH_2$), 2.05–2.43 (3H, m, $CH_2$ and PhCHCH), 2.56 (1H, dd, *J* 13.5, 6.7, $NCH_2$), 2.84 (1H, dd, *J* 13.5, 5.2, $NCH_2$), 3.18 (1H, d, *J* 2.5, PhCH), 3.32–3.48 (1H, m, CHOSi), 4.90–5.15 (4H, m, CH=C$H_2$), 5.75–6.00 (2H, m, CH=$CH_2$), 7.25-–7.40 (5H, m, arom). $^{13}$C NMR: δ 138.8, 135.7, 130.3, 128.0, 127.6, 125.9, 116.5, 114.3, 74.3, 55.0, 47.6, 46.8, 35.5, 29.3, 25.8, 18.0, –4.0, –4.8. MS, *m/z*: 357 ([M]$^+$, 9%), 342 (2), 316 (13), 300 (32), 226 (6), 216 (20), 198 (64), 184 (44), 175 (16), 144 (17), 115 (16), 106 (20), 104 (20), 91 (25). Calcd for $C_{22}H_{35}NOSi$: C, 73.89; H, 9.87; N, 3.92. Found C, 74.15; H, 9.99; N, 3.79.

**Carbonylation of 1,2-dialkenylaziridines (5a-9a, 8b-9b). Typical procedure. –** The aziridine (0.2–0.5 mmol) was dissolved in anhydrous and oxygen-free 1,2-dimethoxyethane (5–10 mL) in a stainless steel pressure vessel equipped with a glass liner and a stirring bar. Dicobalt octacarbonyl was then added (1/12 ratio with the aziridine), the autoclave was purged with carbon monoxide and finally charged with 500 psi CO. After 20 h at 110 °C in an oil bath, the system was cooled to rt and CO was slowly released. The brown clear solution was left to stir in contact with the air and ether (10 mL) was added to favor catalyst decomposition. The cloudy violet suspension thus obtained was filtered on a short Celite® pad, the clear solution was rotary evaporated and purified by column chromatography using the eluant indicated below [in square brackets] to afford the ring-expanded product in pure form.

***trans*-1-Allyl-4-(1-hydroxy-2-propenyl)-3-phenylazetidin-2-one (10a) –** From *cis*-aziridine (**5a**), β-lactam (**10a**) [ether/light petroleum 70:30] was obtained as a yellow oil in 66% yield. $^1$H NMR (200 MHz): δ 1.44 (1H, s, CHOH), 3.68 (1H, dd, *J* 3.2, 2.4, PhCHCH), 3.78 (1H, ddq, *J* 15.4, 7.0, 1.5, $NCH_2$), 4.15 (1H, ddt, *J* 15. 8, 5.7, 1.5, $NCH_2$), 4.31 (1H, d, *J* 2.5, PhCH), 4.48 (1H, m, CHOH), 5.27 (1H, dq, *J* 10.0, 1.5, $NCH_2CH=CH_2$), 5.32 (1H, dq, *J* 18.0, 1.5, $NCH_2CH=CH_2$), 5.32 (1H, dt, *J* 10.0, 1.4, $CHOHCH=CH_2$), 5.47 (1H, dt, *J* 18.0, 1.4, $CHOHCH=CH_2$), 5.77–6.03 (2H, m, $CH=CH_2$), 7.17–7.40 (5H, m, arom). $^{13}$C NMR: δ 167.0, 136,.4, 129.2, 127.9, 127.7, 119.3, 118.4, 71.1, 63.8, 55.5, 44.0, 30.7. MS, *m/z*: 244 ($[M+1]^+$, 2%), 186 (5), 160 (100), 145 (23), 117 (53), 105 (80), 91 (57), 82 (21), 77 (25), 69 (17). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found C, 74.17; H, 7.20; N, 5.81.

***trans*-1-Allyl-4-(1-hydroxy-3-butenyl)-3-phenylazetidin-2-one (11a) –** The title β-lactam was obtained as a yellow oil in 42% yield from carbonylation of *cis*-aziridine (**6a**) [ether/light petroleum 70:30]. $^1$H NMR (200 MHz): δ 2.10–2.50 (3H, m, OH and $CHOHCH_2$), 3.61 (1H, dd, *J* 7.5, 2.4, PhCHCH), 3.76–3.90 (1H, m, CHOH), 3.94 (1H, dd, *J* 15.5, 6.6, $NCH_2$), 3.98 (1H, d, *J* 2.5, PhCH), 4.17 (1H, ddt, *J* 15.5, 5.5, 1.5, $NCH_2$), 5.05–5.37 (4H, m, $CH=CH_2$), 5.68–6.02 (2H, m, $CH=CH_2$), 7.22–7.39 (5H, m, arom). $^{13}$C NMR: δ 167.9, 134.8, 133.1, 132.8, 128.9, 127.6, 127.5, 119.3, 118.3, 73.3, 64.2, 57.1, 44.6, 38.8. MS, *m/z*: 258 ($[M+1]^+$, 11%), 216 (8), 174 (83), 158 (33), 143 (13), 133 (100), 115 (11), 55 (13). Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found C, 74.55; H, 7.29; N, 5.54.

***trans*-1-Allyl-4-(1-hydroxy-4-pentenyl)-3-phenylazetidin-2-one (12a) –** From *cis*-aziridine (**7a**), the title compound [ether/light petroleum 70:30] was obtained as a yellow liquid in 53% yield. $^1$H NMR (200 MHz): δ 1.46–1.70 (2H, m, $CH_2$), 2.04–2.37 (2H, m, $CH_2$), 2.49 (1H, d, *J* 4.9, OH), 3.58 (1H, dd, *J* 7.0, 2.4, PhCHCH), 3.76–3.85 (1H, m, CHOH), 3.85–4.01 (2H, m, $NCH_2$ and PhCH), 4.15 (1H, ddt, *J* 15.6, 5.5, 1.4, $NCH_2$), 4.96–5.11 (2H, m, $CH=CH_2$), 5.20–5.36 (2H, m, $CH=CH_2$), 5.69–6.00 (2H, m, $CH=CH_2$), 7.21–7.42 (5H, m, arom). $^{13}$C NMR: δ 168.2, 137.7, 134.9, 132.9, 128.9, 127.5, 127.4, 118.4, 115.6, 73.5, 64.8, 57.0, 44.6, 33.3, 29.7. MS, *m/z*: 272 ($[M+1]^+$, 30%), 188 (16), 170 (18), 146 (14), 133 (100), 115 (23), 105 (63), 91 (35), 83 (14). Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found C, 75.38; H, 7.92; N, 5.04.

***trans*-1-Allyl-4-(1-*tert*-butyldimethylsilyloxy-3-butenyl)-3-phenylazetidin-2-one (13a) –** From *cis*-aziridine (**8a**), β-lactam (**13a**) [ether/light petroleum 50:50] was obtained as a yellow oil in 63% yield. $^1$H NMR (200 MHz): δ 0.10 (3H, s, $^t$BuMe$_2$Si), 0.13 (3H, s, $^t$BuMe$_2$Si), 0.92 (9H, s, $^t$BuMe$_2$Si), 2.39 (2H, m, $SiOCHCH_2CH=$), 3.72 (1H, dd, *J* 4.3, 2.4, PhCHCH), 3.73 (1H, ddq, *J* 15.7, 6.8, 1.0, $NCH_2$), 4.00 (1H, dt, *J* 4.6, 5.9, CHOSi), 4.09 (1H, d, *J* 2.4, PhCH), 4.26 (1H, ddt, *J* 15.7, 5.2, 1.6, $NCH_2$), 4.93–5.09 (2H, m, $CH=CH_2$), 5.21–5.35 (2H, m, $CH=CH_2$), 5.66–5.99 (2H, m, $CH=CH_2$), 7.20–7.39 (5H, m, arom).

$^{13}$C NMR: δ 169.7, 136.7, 134.9, 133.8, 130.1, 128.9, 128.7, 119.7, 119.6, 74.0,64.0, 58.1, 45.6, 40.1, 27.2, 1.4, –2.7, –3.2. MS, *m/z*: 370 ([M–1]$^+$, 2%), 330 (3), 314 (2), 286 (2), 248 (23), 247 (100), 231 (6), 196 (45), 155 (7), 115 (13), 75 (21), 73 (44). Anal. Calcd for $C_{22}H_{33}NO_2Si$: C, 71.11; H, 8.95; N, 3.77. Found C, 71.25; H, 9.12; N, 3.69.

***trans*-1-Allyl-4-(1-*tert*-butyldimethylsilyloxy-4-pentenyl)-3-phenylazetidin-2-one (14a) –** Carbonylation of *cis*-aziridine (**9a**) afforded the title β-lactam [light petroleum/ether 70:30] as a yellow oil in 21% yield. $^1$H NMR (200 MHz): δ 0.11 (3H, s, $^t$Bu$\underline{\text{Me}}_2$Si), 0.13 (3H, s, $^t$Bu$\underline{\text{Me}}_2$Si), 0.94 (9H, s, $^t\underline{\text{Bu}}$Me$_2$Si), 1.48–1.74 (2H, m, $CH_2$), 2.01–2.18 (2H, m, $CH_2$), 3.47 (1H, ddq, *J* 15.6, 6.4, 1.0, $NCH_2$), 3.67 (1H, t, *J* 2.1, PhCHC$\underline{\text{H}}$), 4.01 (1H, td, *J* 5.9, 1.7, CHOSi), 4.25–4.40 (2H, m, $NCH_2$ and PhC$\underline{\text{H}}$), 4.90–5.03 (2H, m, CH=C$\underline{\text{H}}_2$), 5.20–5.32 (2H, m, CH=C$\underline{\text{H}}_2$), 5.63–5.96 (2H, m, C$\underline{\text{H}}$=CH$_2$), 7.24–7.42 (5H, m, arom). $^{13}$C NMR: δ 168.1, 137.6, 132.1, 128.8, 127.6, 127.3, 118.6, 115.2, 68.7, 63.2, 54.9, 43.2, 33.9, 29.7, 29.4, 25.8, –4.8, –5.0. MS, *m/z*: 385 (M$^+$, 1%), 302 (9), 247 (54), 245 (76), 210 (100), 167 (16), 168 (20), 129 (27), 115 (23), 75 (91), 73 (59). Anal. Calcd for $C_{23}H_{35}NO_2Si$: C, 71.64; H, 9.15; N, 3.63. Found C, 71.71; H, 9.30; N, 3.86.

**Ring-closing metathesis (RCM) cyclizations. Typical procedure –** The 1,4-dialkenyl-β-lactam (0.284 mmol) was dissolved in 10 mL of anhydrous and degassed dichloromethane in a 50-mL Schlenk flask. Grubbs' catalyst **I** (0.028 mmol) was added under argon flow and the brownish-violet solution was stirred at room temperature under inert atmosphere. After 21 h, the flask was opened and the mixture exposed to air under vigorous stirring for a couple of hours to favour catalyst decomposition. The mixture was then evaporated to dryness under reduced pressure and purified by column chromatography using the eluant indicated below [in square brackets].

***trans*-5-Hydroxy-7-phenyl-1-azabicyclo[4.2.0]oct-3-en-8-one (15a) –** Ring-closing metathesis of **10a** afforded bicyclic product (**15a**) [ether/light petroleum 70:30] as a yellow oil in 73% yield. $^1$H NMR (200 MHz): δ 1.44 (1H, s, CHO$\underline{\text{H}}$), 3.31 (1H, dd, *J* 7.5, 1.1, PhCHC$\underline{\text{H}}$), 3.55 (1H, dd, *J* 19.0, 1.5, $NCH_2$), 4.08 (1H, br d, *J* 19.0, $NCH_2$), 4.16 (1H, br s, PhC$\underline{\text{H}}$), 4.32 (1H, t, *J* 6.7, C$\underline{\text{H}}$OH), 5.70–5.90 (2H, m, C$\underline{\text{H}}$=C$\underline{\text{H}}$), 7.20–7.42 (5H, m, arom). $^{13}$C NMR: δ 168.4, 135.6, 133.0, 131.2, 129.5, 128.0, 124.2, 69.2, 63.2, 38.8, 31.3. MS, *m/z*: 215 ([M]$^+$, 4%), 198 (5), 196 (1),172 (100), 159 (12), 143 (9), 128 (14), 124 (24), 105 (25), 91 (69), 77 (25), 68 (16), 55 (10). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found C, 72.73; H, 5.98; N, 6.63.

***trans*-6-Hydroxy-8-phenyl-1-azabicyclo[5.2.0]non-3-en-9-one (16a) –** After chromatographic purification [ether/light petroleum 90:10], the title compound was obtained from *trans*-β-lactam (**11a**) as

a yellow oil in 50% yield. $^1$H NMR (200 MHz): δ 2.20 (1H, br s, OH), 2.32–2.50 (1H, m, CHOHC<u>H</u>$_2$CH=), 2.80 (1H, dt, *J* 16.7, 6.6, CHOHC<u>H</u>$_2$CH=), 3.65 (1H, m, NCH$_2$), 3.84 (1H, t, *J* 2.4, PhCHC<u>H</u>), 4.22 (1H, br s, C<u>H</u>OH), 4.48 (1H, d, *J* 2.4, PhC<u>H</u>), 4.52 (1H, dd, *J* 17.2, 5.4, NCH$_2$), 5.56–5.82 (2H, m, C<u>H</u>=C<u>H</u>), 7.21–7.40 (5H, m, arom). $^{13}$C NMR: δ 168.1, 128.8, 128.0, 127.5, 127.4, 125.1, 67.3, 66.2, 56.7, 40.9, 33.5. MS, *m/z*: 229 (M$^+$, 2%), 134 (10), 133 (100), 118 (3), 115 (16), 105 (7), 91 (8), 77 (7), 55 (18). Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found C, 73.21; H, 6.71; N, 6.31.

***trans*-7-Hydroxy-9-phenyl-1-azabicyclo[6.2.0]dec-3-en-10-one (17a) –** RCM of **12a** provided fused β-lactam (**17a**) [ether/light petroleum 90:10] in 88% yield. $^1$H NMR (200 MHz): δ 1.45–2.50 (4H, m, CH$_2$), 2.98 (1H, br s, -OH), 3.80–4.23 (4H, m, NCH$_2$, PhCHC<u>H</u> and C<u>H</u>OH), 3.66 (1H, d, *J* 2.2, PhC<u>H</u>), 5.64–5.83 (1H, m, CH=), 6.11 (1H, q, *J* 8.8, CH=), 7.18–7.38 (5H, m, arom). $^{13}$C NMR: δ 167.7, 138.0, 128.9, 128.8, 127.4, 127.3, 123.2, 68.7, 64.1, 55.8, 36.8, 35.2, 31.9. MS, *m/z*: 244 ([M+1]$^+$, 2%), 243 (7), 215 (2), 133 (100), 115 (33), 105 (56), 104 (48), 91 (42), 77 (24), 68 (25), 55 (27). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found C, 74.21; H, 7.11; N, 5.66.

***trans*-6-*tert*-Butyldimethylsilyloxy-8-phenyl-1-azabicyclo[5.2.0]non-3-en-9-one (18a) –** The title compound was obtained as a dark oil from *trans*-β-lactam (**13a**) in 66% yield after chromatographic purification [diethyl ether/light petroleum 70:30]. $^1$H NMR (200 MHz): δ 0.04 (3H, s, $^t$Bu<u>Me</u>$_2$Si), 0.09 (3H, s, $^t$Bu<u>Me</u>$_2$Si), 0.89 (9H, s, $^t$<u>Bu</u>Me$_2$Si), 2.21 (1H, ddd, *J* 16.2, 6.6, 2.2, SiOCHC<u>H</u>$_2$CH=), 2.58–2.78 (1H, m, SiOCHC<u>H</u>$_2$CH=), 3.50–3.65 (1H, m, NCH$_2$), 3.83 (1H, dd, *J* 4.5, 2.0, PhCHC<u>H</u>), 4.27 (1H, ddd, *J* 9.5, 4.6, 2.3, CHOSi), 4.35 (1H, d, *J* 2.0, PhC<u>H</u>), 4.41–4.56 (1H, m, NCH$_2$), 5.47–5.72 (2H, m, CH=), 7.19–7.35 (5H, m, arom). $^{13}$C NMR: δ 169.3, 137.0, 130.0, 129.1, 128.6, 128.2, 126.4, 71.5, 66.3, 57.4, 42.8, 33.9, 27.1, 19.4, –3.4, –3.5. MS, *m/z*: 286 ([M–15]$^+$, 2%), 287 (3), 286 (15), 248 (19), 247 (100), 232 (9), 210 (2), 189 (5), 168 (20), 166 (9), 115 (9), 100 (6), 91 (8), 73 (36). Anal. Calcd for $C_{20}H_{29}NO_2Si$: C, 69.92; H, 8.51; N, 4.08. Found C, 70.09; H, 8.62; N, 4.20.

***trans*-7-tert-Butyldimethylsilyloxy-9-phenyl-1-azabicyclo[6.2.0]dec-3-en-10-one (19a) –** RCM of **14a** gave the title bicyclic β-lactam [ether/light petroleum 70:30] as a dark oil in 70% yield. $^1$H NMR (200 MHz): δ 0.10 (3H, s, $^t$Bu<u>Me</u>$_2$Si), 0.11 (3H, s, $^t$Bu<u>Me</u>$_2$Si), 0.89 (9H, s, $^t$<u>Bu</u>Me$_2$Si), 1.50–2.50 (4H, m, CH$_2$), 3.66 (1H, dd, *J* 8.9, 2.1, PhCHC<u>H</u>), 3.71–3.83 (1H, m, CHOSi), 3.86 (1H, dd, *J* 14.5, 7.1, NCH$_2$), 4.03 (1H, dd, *J* 14.5, 7.6, NCH$_2$), 4.10 (1H, d, *J* 2.1, PhC<u>H</u>), 5.73 (1H, dt, *J* 10.2, 7.2, CH=), 5.95 (1H, dt, *J* 10.2, 7.9, CH=), 7.23–7.43 (5H, m, arom). $^{13}$C NMR: δ 165.5, 135.8, 128.4, 127.6, 127.0, 123.1, 75.3, 65.6, 57.1, 36.3, 36.0, 25.8, 22.5, –4.2, –4.4. MS, *m/z*: 357 (M$^+$, 2%), 301 (23), 300 (100), 257 (29), 247 (49), 183 (30), 155 (38), 141 (60), 129 (50), 117 (48), 115 (49), 91 (70), 75 (71), 73 (83), 57 (83). Anal. Calcd for $C_{21}H_{31}NO_2Si$: C, 70.54; H, 8.74; N, 3.92. Found C, 70.71; H, 8.65; N, 3.98.

**2-[3-(*tert*-Butyldimethylsilyloxy)-1-phenylhexa-1,5-dienyl]-5,6-dihydro-4*H*-[1,3]oxazine (20b)** – Carbonylation of *trans*-aziridine (**8b**) afforded the title compound in 17% total yield as a mixture of *E*/*Z* stereoisomers in 70:30 ratio, which were separated by chromatography [ether/light petroleum 70:30].

*1st eluted*: oil; $^1$H NMR (200 MHz): δ 0.13 (3H, s, $^t$Bu$\underline{\text{Me}}_2$Si), 0.14 (3H, s, $^t$Bu$\underline{\text{Me}}_2$Si), 0.95 (9H, s, $^t\underline{\text{Bu}}$Me$_2$Si), 1.85–2.10 (2H, m, CH$_2$C$\underline{\text{H}}_2$CH$_2$), 2.18–2.50 (4H, m, C$\underline{\text{H}}_2$CH=CH$_2$ and NCH$_2$), 3.33 (2H, dt, *J* 7.1, 3.0, CH$_2$O), 4.71 (1H, ddd, *J* 6.1, 4.6, 1.2, CHOSi), 4.98–5.15 (2H, m, C$\underline{\text{H}}_2$=CH), 5.78–6.01 (1H, m, CH$_2$=C$\underline{\text{H}}$), 6.67 (1H, s, PhC=C$\underline{\text{H}}$), 7.20–7.40 (5H, m, arom). Anal. Calcd for $C_{22}H_{33}NO_2Si$: C, 71.11; H, 8.95; N, 3.77. Found C, 71.02; H, 9.05; N, 3.81.

*2nd eluted*: oil; $^1$H NMR (200 MHz): δ –0.21 (3H, s, $^t$Bu$\underline{\text{Me}}_2$Si), –0.18 (3H, s, $^t$Bu$\underline{\text{Me}}_2$Si), 0.81 (9H, s, $^t\underline{\text{Bu}}$Me$_2$Si), 1.55–1.85 (2H, m, C$\underline{\text{H}}_2$CHOSi), 1.95–2.20 (2H, m, CH$_2$C$\underline{\text{H}}_2$CH$_2$), 2.35–2.55 (2H, m, NCH$_2$), 3.64 (1H, dt, *J* 10.3, 6.9, CH$_2$O), 4.02 (1H, dt, *J* 10.3, 6.9, CH$_2$O), 4.88 (1H, t, *J* 6.3, CHOSi), 5.03–5.18 (2H, m, C$\underline{\text{H}}_2$=CH), 5.85 (1H, ddt, *J* 17.8, 10.3, 7.0, CH$_2$=C$\underline{\text{H}}$), 6.66 (1H, s, PhC=C$\underline{\text{H}}$), 7.20–7.45 (5H, m, arom). Anal. Calcd for $C_{22}H_{33}NO_2Si$: C, 71.11; H, 8.95; N, 3.77. Found C, 71.27; H, 9.11; N, 3.89.

**2-[3-(*tert*-Butyldimethylsilyloxy)-1-phenylhepta-1,6-dienyl]-5,6-dihydro-4*H*-[1,3]oxazine (21b)** – Similarly as above, carbonylation of *trans*-aziridine (**9b**) provided the title oxazine in 38% overall yield as a 60:40 mixture of *E*/*Z* stereoisomers which were amenable to separation by column chromatography [ether/light petroleum 50:50].

*1st eluted*: oil; $^1$H NMR (200 MHz): δ 0.14 (3H, s, $^t$Bu$\underline{\text{Me}}_2$Si), 0.15 (3H, s, $^t$Bu$\underline{\text{Me}}_2$Si), 0.96 (9H, s, $^t\underline{\text{Bu}}$Me$_2$Si), 1.48–1.83 (2H, m, C$\underline{\text{H}}_2$CHOSi), 1.88–2.11 (2H, m, CH$_2$C$\underline{\text{H}}_2$CH$_2$), 2.12–2.26 (2H, m, CH$_2$=CHC$\underline{\text{H}}_2$), 2.32–2.45 (2H, m, NCH$_2$), 3.29–3.42 (2H, m, CH$_2$O), 4.64 (1H, ddd, *J* 6.7, 4.3, 1.1, CHOSi), 4.92–5.09 (2H, m, C$\underline{\text{H}}_2$=CH), 5.85 (1H, ddt, *J* 17.1, 10.2, 6.5, CH$_2$=C$\underline{\text{H}}$), 6.65 (1H, s, PhC=C$\underline{\text{H}}$), 7.18–7.38 (5H, m, arom). $^{13}$C NMR: δ 175.0, 138.6, 128.4, 127.9, 127.4, 124.6, 114.5, 72.0, 48.8, 35.2, 31.2, 29.3, 25.9, 19.4, –4.4, –5.0. MS, *m/z*: 384 ([M–1]$^+$, 1%), 370 (3), 344 (3), 330 (9), 329 (23), 328 (100), 302 (7), 272 (5), 212 (7), 142 (20), 128 (10), 115 (12), 75 (23), 73 (29). Anal. Calcd for $C_{23}H_{35}NO_2Si$: C, 71.64; H, 9.15; N, 3.63. Found C, 71.59; H, 9.21; N, 3.72.

*2nd eluted*: oil; $^1$H NMR (200 MHz): δ –0.20 (3H, s, $^t$Bu$\underline{\text{Me}}_2$Si), –0.12 (3H, s, $^t$Bu$\underline{\text{Me}}_2$Si), 0.84 (9H, s, $^t\underline{\text{Bu}}$Me$_2$Si), 1.64-1.80 (2H, m, C$\underline{\text{H}}_2$CHOSi), 1.97–2.22 (4H, m, CH$_2$C$\underline{\text{H}}_2$CH$_2$ and CH$_2$=CHC$\underline{\text{H}}_2$), 2.38–2.55 (2H, m, NCH$_2$), 3.63 (1H, dt, *J* 10.5, 6.9, OCH$_2$), 4.01 (1H, dt, *J* 10.5, 6.9, OCH$_2$), 4.85 (1H, t, *J* 6.7, CHOSi), 4.90–5.06 (2H, m, C$\underline{\text{H}}_2$=CH), 5.85 (1H, ddt, *J* 17.0, 10.3, 6.5, CH$_2$=C$\underline{\text{H}}$), 6.66 (1H, s, PhC=C$\underline{\text{H}}$), 7.20–7.45 (5H, m, arom). $^{13}$C NMR: δ 138.2, 129.0, 128.8, 128.1, 127.2, 114.7, 69.0, 51.2, 35.2, 31.4, 29.8, 25.7, 18.8, –4.6, –5.4. MS, *m/z*: 384 ([M–1]$^+$, 1%), 370 (2), 344 (2), 330 (10), 329 (18), 328 (82), 302 (5), 272 (4), 212 (12), 142 (39), 128 (26), 115 (30), 75 (63), 73 (100). Anal. Calcd for $C_{23}H_{35}NO_2Si$: C, 71.64; H, 9.15; N, 3.63. Found C, 71.85; H, 9.32; N, 3.79.

**ACKNOWLEDGEMENTS**

We thank Ministero dell'Istruzione, dell'Università e della Ricerca (MIUR) for financial support (COFIN 2001). A.S. thanks MIUR for a doctoral fellowship. Spectroscopical assistance from Centro Interdipartimentale Grandi Strumenti (Università di Modena e Reggio Emilia) has been greatly appreciated. We are grateful to Prof. A.C. Fabretti (Dipartimento di Chimica) for kindly providing dry-box facilities. Thanks are due to Professor Irene Moretti, to whom this paper is dedicated, for her continuous encouragement and committment throughout the years in the field of heterocyclic chemistry.

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