Synthesis and Aza-[2,3]-Wittig Rearrangements of Vinylaziridines: Scope and Limitations

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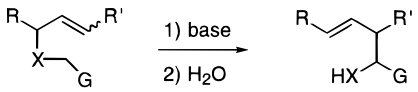
cis- and *trans*-2,3-Trisubstituted vinylaziridines have been prepared from *cis*- and *trans*-epoxy alcohols, respectively, and used as substrates in the aza-[2,3]-Wittig rearrangement. Five different anion-stabilizing groups have been investigated for their efficiency to promote the rearrangement, and it was found that *N*-*tert*-butyl acetyl vinylaziridines were superior in this reaction, affording the corresponding *cis*-2,6-tetrahydropyridines (>90%) as single isomers when treated with LDA. Similarly, the corresponding (*Z*)-propenylaziridines gave *trans*,*trans*-2,3,6-trisubstituted tetrahydropyridines as the sole products while the (*E*)-propenylaziridines afforded the *cis*,*cis*-2,3,6-derivatives with equally high selectivity. The scope and limitations of the process have been investigated by varying the structure of the substrate, and the mechanism of the rearrangement has been probed to some extent; the mechanistic picture is more complex than assumed previously.

Introduction

Pericyclic reactions are an important cornerstone in organic synthesis, due mainly to their predictability and often high selectivities. A good example is the sigmatropic [2,3]-Wittig rearrangement, in which an activated allylic ether is transformed into the corresponding homoallylic alcohol (eq 1, X = O). This reaction has received much attention from both synthetic and computational chemists, and its potential has been demonstrated by its use as a key step in several natural product syntheses.[1] The rearrangement is generally considered to proceed by a concerted mechanism, passing through a five-membered envelopelike transition state in which the breaking C−O and forming C−C bonds are almost eclipsed.[2,3] The diastereoselectivities observed in this process are then a direct consequence of the starting olefin geometry and the preference of the activating group (G) to adopt an *endo* or an *exo* orientation in the transition state, the reasons for which have been shown to be of primarily electronic origin. It has also been demonstrated that the [2,3]-Wittig rearrangement can be performed with excellent 1,3- or 1,4-chirality transfer and that high asymmetric induction can be achieved by the use of chiral auxiliaries.[1]



(1)

X=O, NR"
G=Ph, CO_2R, C≡CTMS, CN, ...

Somewhat surprisingly, however, the corresponding aza-[2,3]-Wittig rearrangement (eq 1, X = NR″) has received considerably less attention. At the outset of this investigation only a few attempts in this area had been made which indicated that these systems tend to be unreactive or are prone to undergo a competitive [1,2]- rather than the desired [2,3]-rearrangement.[4,5] However, in an elegant study Durst *et al.* showed that *N*-benzyl-4-vinyl-2-azetidinone when treated with LDA was transformed into the corresponding seven-membered lactam in high yield.[6] It was also noted by these authors that the ease with which this aza-[2,3]-Wittig rearrangement occurred undoubtedly was associated with the considerable relief of ring strain in going from a four- to a seven-membered ring. Following this key observation we became interested in the possibility of using *N*-substituted vinylaziridines as substrates for this rearrangement which would result in a novel entry to di- and trisubstituted tetrahydropyridines (eq 2).[7] In two preliminary reports we have shown that the required vinylaziridines are readily prepared in high enantiomeric excess from epoxy alcohols and that, when deprotonated by base, they rearrange to the corresponding tetrahydropyridines. The yield and relative stereochemistry of the products depend on the vinylaziridine geometry and the nature of the *N*-activating group.[8] In a parallel study the potential of this rearrangement was demonstrated by using it as a key step in our enantioselective synthesis of (−)-Indolizidines 209B and 209D, two alkaloids that have been isolated in minute quantities from *Dendrobatidae* frogs.[9] Herein we give a detailed account of the preparation of various *N*-substituted vinylaziridines and their subsequent rearrangement which shows the scope and limitations of the process, both in terms of activating groups and the structure of the substrate. In addition,

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(2) (a) Mikami, K.; Uchida, T.; Hirano, T.; Wu, Y.-D.; Houk, K. N. *Tetrahedron* **1994**, *50*, 5917. (b) Wu, Y.-D.; Houk, K. N.; Marshall, J. A. *J. Org. Chem.* **1990**, *55*, 1421-1423.

(3) For a somewhat different transition state structure, see ref 1c.

(4) (a) Reetz, M. T.; Schinzer, D. *Tetrahedron Lett.* **1975**, 3485−3486. (b) Broka, C. A.; Shen, T. *J. Am. Chem. Soc.* **1989**, *111*, 2981−2984. (c) Murata, Y.; Nakai, T. *Chem. Lett.* **1990**, 2069−2072. (d) Coldham, I. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1275−1276.

(5) The rearrangement described in ref 4b has been shown to proceed by a [1,2]-mechanism, see ref 4c.

(6) Durst, T.; Elzen, R. V. D.; LeBelle, M. J. *J. Am. Chem. Soc.* **1972**, *94*, 9261-9263.

(7) The ring strain in ethylenimine has been assessed to 26.9 kcal/mol. Dermer, O. C.; Ham, G. E. *Ethylenimine and Other Aziridines*; Academic: New York, 1969; p 89.

(8) Åhman, J.; Somfai, P. *J. Am. Chem. Soc.* **1994**, *116*, 9781−9782. Åhman, J.; Somfai, P. *Tetrahedron Lett.* **1996**, *37*, 2495−2498.

(9) Åhman, J.; Somfai, P. *Tetrahedron Lett.* **1995**, *36*, 303−306. Åhman, J.; Somfai, P. *Tetrahedron* **1995**, *51*, 9747−9756.

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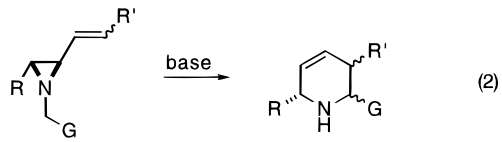
the mechanistic aspects of this reaction have been probed to some extent by systematically varying the structure of the vinylaziridines.



(2)

R'=H, alkyl

During the course of this investigation three other studies of the aza-[2,3]-Wittig rearrangement have appeared. The Coldham group has also described the use of vinylaziridines, prepared in racemic form by a conjugate addition strategy, as substrates in the rearrangement and obtained results similar to our preliminary ones.[10] Anderson *et al*.[11] recently described the successful [2,3]-rearrangement of an allylic Boc-protected benzylamine, which seems to indicate a fruitful approach for the rearrangement of acyclic substrates, while Gawley *et al*. rearranged 2-lithio-*N*-allylpyrrolidines and showed that this reaction proceeds with inversion of configuration at the lithium-bearing carbon, in analogy with the original Wittig rearrangement.[12]

Results and Discussion

Synthesis of Vinylaziridines. Vinylaziridines have received interest as precursors for a variety of nitrogen-containing compounds and as a result several strategies toward them have been described.[13] The main thrust in this area has been directed toward addition of azides[14] or nitrene equivalents[15] to 1,3-dienes, with attendant problems with regioselectivity, while other methods such as derivatization of vinyl epoxides,[16] intramolecular S_N2' substitutions,[17] reduction or alkylation of α,β-unsaturated oximes,[18] and nucleophilic additions to oximes have also been described.[19] With respect to the present investigation the main drawback with most of these methods are the need to use a nitrogen protecting group and the fact that they are not easily amenable to the preparation of vinylaziridines of high enantiomeric purity. However, Wittig olefination of various *N*-alkylated[20] or tosylated[21] 2-formylaziridines has been described, and since these compounds should be readily available from Sharpless epoxy alcohols this route was judged to be ideal for our purposes. Thus, opening of the known epoxides **1**[22] and **2**[23] (ee >95%) with sodium azide[24] followed by selective protection of the primary hydroxyl group gave the corresponding vicinal azido alcohols (Scheme 1). These were then subjected to Ph_3P in refluxing toluene to give aziridines **3** and **5**, each as a single isomer.[25] It has previously been shown that this aziridination proceeds *via* an intermediate oxazaphospholidine which decomposes and undergoes intramolecular S_N2 displacement of Ph_3PO with concomitant formation of the aziridine, its stereochemistry thus being inverted as compared to the starting epoxide.[26]

N-Alkylation of **3** with *tert*-butyl bromoacetate[27] gave aziridine **6**, and subsequent removal of the silyl group afforded alcohol **11** in good overall yield. Oxidation of **11** was best accomplished by using the Swern protocol,[28] and condensation of the resultant aldehyde with the ylides derived from methyl- and ethyltriphenylphosphonium bromide (KHMDS, PhMe, THF) gave vinylaziridines **17** and **18**, while the (*E*)-isomer **19** was prepared from the same aldehyde by applying the Schlosser modification of the Wittig olefination.[29] Similarly, aziridine **20** was made by the *in situ* condensation of the aldehyde derived from **11** with Ph_3PCHCO_2Et[30] while aziridine **22** was prepared by reacting the same aldehyde with $Ph_3PCHCHO$ to give **21a** followed by reduction ($NaBH_4$, 90%) and silylation (99%). *N*-Alkylation of **3** with benzyl bromide, bromoacetonitrile, or propargyl bromide under standard conditions gave compounds **7**−**9** which were converted into vinylaziridines **23**−**25**, **27**, and **29** by using the procedures described above for **17**−**19**. The TMS-derivatives **26**, **28**, and **30** were most conveniently prepared by deprotonation of **25**, **27**, and **29** with *n*-BuLi at −78 °C followed by addition of TMSCl. For the preparation of vinylaziridine **31**, silyl ether **3** was deprotected to give alcohol **4** which was alkylated with methyl 4-bromocrotonate (83%) to give **15** which was then oxidized and methylenated as described above. Finally, vinylaziridines **32**−**34** were prepared from **5** by following the analogous sequence of reactions as for compounds **17**−**19**. Included in this study are also derivatives **35** and **36** the preparation of which has been previously described.[9] Since it was noted that several of these *trans*-

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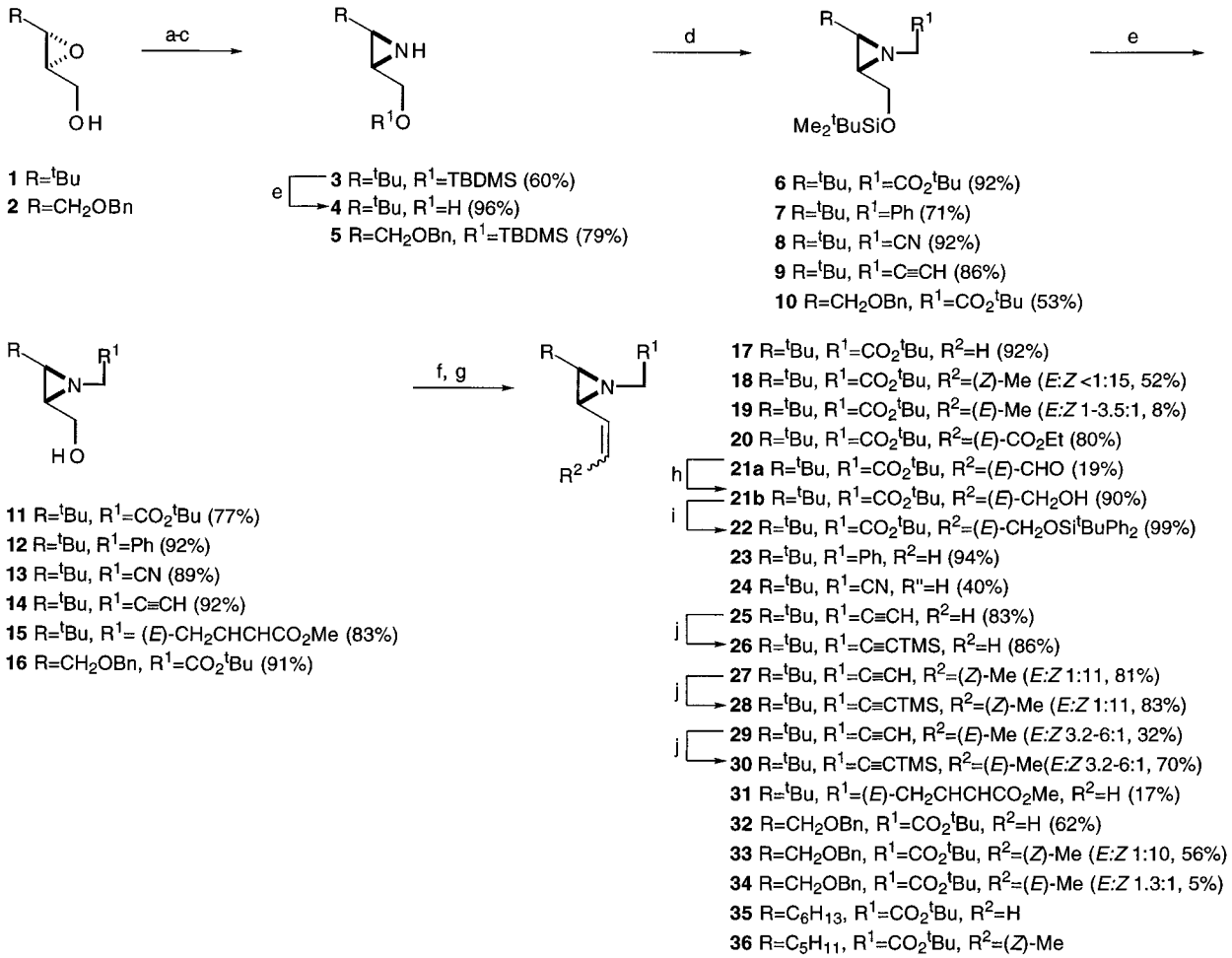
Scheme 1[a]



[a] Conditions: (a) NaN_3, $MeO(CH_2)_2OH$, H_2O, reflux; (b) *t*-$BuMe_2SiCl$, Et_3N, DMAP, CH_2Cl_2; (c) Ph_3P, PhMe, reflux; (d) $R'CH_2Br$, K_2CO_3, 18-crown-6, THF, rt; (e) Bu_4NF, THF, 0 °C; (f) $(COCl)_2$, DMSO, Et_3N, −78 °C; (g) Ph_3PCH_3Br, KHMDS, THF, −15 °C (for **17**, **23**−**25**, **31**, **32**); $Ph_3PCH_2CH_3Br$, KHMDS, THF, −15 °C (for **18**, **27**, **33**); $Ph_3PCH_2CH_3Br$, PhLi, MeOH, PhMe, −30 °C (for **19**, **29**, **34**); Ph_3PCHCO_2Et, CH_2Cl_2, −78 °C → rt (for **20**); $Ph_3PCHCHO$, PhMe, rt (for **21a**); (h) $NaBH_4$, EtOH, −30 °C; (i) *t*-$BuPh_2SiCl$, Et_3N, DMAP, CH_2Cl_2; (j) *n*-BuLi, TMSCl, THF, −78 °C.

2,3-trisubstituted vinylaziridines were prone to undergo thermal [1,5]-hydrogen shifts, these compounds were prepared and processed as quickly as possible, avoiding any prolonged storage or handling at or above room temperature.[31]

In a similar way the *cis*-2,3-trisubstituted vinylaziridines **41**−**43** were prepared in racemic form from epoxy alcohol **37**[32] by following the procedures established for corresponding *trans*-derivatives **32**−**34** (Scheme 2). As can be seen the present route provides (*Z*)-propenyl and vinylaziridines in reasonable overall yields and with good to excellent control over the olefin stereochemistry in the former case (Schemes 1 and 2). However, it is noteworthy that in all cases studied so far the corresponding (*E*)-propenyl derivatives could be obtained only in poor yields with, at best, modest *E*:*Z* selectivity. Although varying degrees of selectivity have previously been observed in the Schlosser olefination, the low yields obtained were surprising, but the cause could be traced to a competitive attack of PhLi on the ester moiety. The (*E*)-propenylaziridines **19**, **30**, **34**, and **43** are included in this study only in order to probe the various mechanistic possibilities in the aza-[2,3]-Wittig rearrangement (*vide infra*).

The ^1H NMR spectra of aziridines **17**−**31** and **41**−**43** all indicate the presence of a single nitrogen invertomer, and it is reasonable to assume that the nitrogen substituent occupies the sterically less hindered position in each case, i.e. *trans* to the *tert*-butyl substituent in compounds **17**−**31** and *trans* to the (benzyloxy)methylene and vinyl substituents in **41**−**43**. This notion was also substantiated by performing a NOESY experiment on vinylaziridine **17** which showed an interaction between the α-carbonyl protons and *t*-Bu*CH* and *CH*CH_2 while a similar experiment with **42** showed an interaction between the α-carbonyl protons and both of the aziridine methine protons. In contrast to this the spectra of vinylaziridines **32**−**36** consist of two sets of lines in a ratio of 2−4:1 at room temperature, indicating an equilibrium of two invertomers. By performing a line-shape analysis on the ^1H NMR spectrum of **32** its barrier for inversion was calculated to be $\Delta G^{\ddagger} = 16.5$ kcal/mol (major

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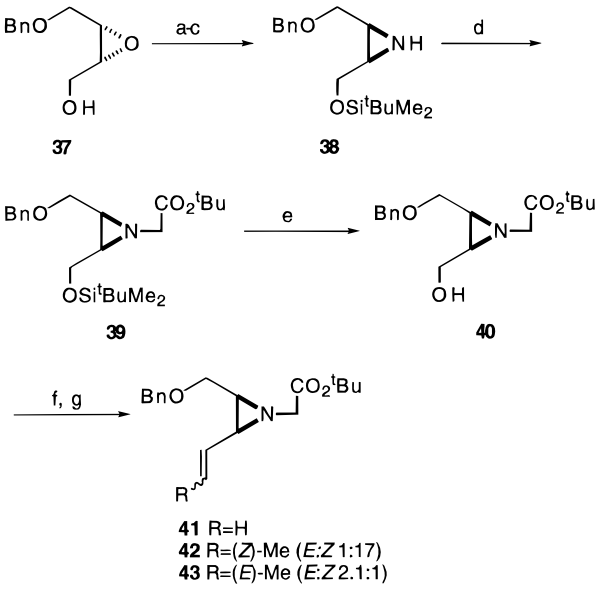
Scheme 2[a]



[a] Conditions: (a) NaN_3, $MeO(CH_2)_2OH$, H_2O, reflux, 97%; (b) *t*-$BuMe_2SiCl$, Et_3N, DMAP, CH_2Cl_2, 85%; (c) Ph_3P, PhMe, reflux, 59%; (d) $BrCH_2CO_2t$-Bu, K_2CO_3, 18-crown-6, THF, rt, 87%; (e) Bu_4NF, THF, 0 °C, 98%; (f) $(COCl)_2$, DMSO, Et_3N, −78 °C; (g) Ph_3PCH_3Br, KHMDS, THF, 0 °C, 92% (for **41**); $Ph_3PCH_2CH_3Br$, KHMDS, THF, −15 °C, 87% (for **42**); $Ph_3PCH_2CH_3Br$, PhLi, MeOH, PhMe, −30 °C, 4% (for **43**).

→ minor) while the difference in free-energy between the invertomers was found to be $\Delta G° = 0.77$ kcal/mol,[33] which is in agreement with literature values for similar compounds.[34]

Rearrangement of Vinylaziridines. The influence of the activating group on the [2,3]-rearrangement, in terms of both reaction outcome and selectivity, is summarized in Table 1. Subjecting vinylaziridine **17** to LDA in THF at −78 °C resulted in the rapid (<5 min) formation of tetrahydropyridine **44** as a single detectable diastereomer (^{1}H NMR). The relative stereochemistry of **44** was assigned by analyzing the relevant coupling constants in its ^{1}H NMR spectrum assuming that the unsaturated six-membered ring adopts a half-chair conformation in which the *tert*-butyl moiety functions as a conformational lock and occupies a pseudoequatorial position. Support for this assignment was obtained by hydrogenation (H_2, Pd/C, EtOH) of **44** to yield the corresponding *cis*-2,6-disubstituted piperidine derivative as evident from its spectral data.[35] The high selectivity observed in the rearrangement of vinylaziridine **17** is gratifying and presents a novel entry to *cis*-2,6-disubstituted piperidine alkaloids.[9] It should also be noted that tetrahydropyridine **44**, as well as the other rearrangement products described in this paper, are not stable to chromatography or storage. However, the produts from these rearrangements are normally pure (>95%), as determined from their ^{1}H NMR spectra, and the yields and ratios reported refer to such crude products. It has been shown that the activating, anion-stabilizing group (eq 1, G) has a decisive effect on the stereochemical outcome of the [2,3]-Wittig rearrangement of allylic ethers, and this obviously raises the question if similar control could be obtained for the title reaction,[1] i.e. if *trans*-2,6-disubstituted tetrahydropyridines could be formed by simply changing the *N*-substituent in the starting vinylaziridine. Therefore nitrile derivative **24** was subjected to LDA (THF, −78 °C) but this gave, somewhat surprisingly, only recovered starting material. This problem was solved by using instead freshly prepared KHMDS as base,[36] resulting in the formation of the corresponding tetrahydropyridines as a mixture of diastereomers (**45**:**46** 6.6:1, 80%). Some decomposed material, presumably the result of a facile elimination of cyanide ion from the initially formed product, was also obtained. Although we were pleased to observe that the rearrangement did indeed proceed, the lower selectivity obtained together with the instability of **45** and **46** toward elimination discouraged further investigations with this particular anion-stabilizing group. Instead our attention was drawn to the fact that α-alkoxy anions derived from allylic propargyl ethers participate in the [2,3]-rearrangement to give homoallylic ethers with the opposite sense of stereoinduction as compared to the corresponding α-alkoxy enolates.[1,37] Accordingly, *N*-propargyl vinylaziridine **25** was selected as the next rearrangement precursor. However, attempts to rearrange **25** by using *n*-BuLi, *n*-BuLi/TMEDA or *s*-BuLi (3 equiv, THF) gave none of the expected tetrahydropyridines and **25** was recovered unchanged, or with complete incorporation of deuterium at the terminal alkyne position when the reaction was quenched with D_2O. This is in contrast to the behavior of allylic propargyl ethers which are smoothly deprotonated by the action of *n*-BuLi.[37,38] However, subjecting the TMS derivative **26** to *s*-BuLi (THF, −78 °C) resulted in the formation of the *cis*-2,6- and *trans*-2,6-disubstituted tetrahydropyridines **47** and **48** along with considerable amounts of 1-pyrroline **49** (**47**:**48**:**49** 1.2:1.8:1, 95% total yield). The relative stereochemistry of **47** and **48** was assigned by inspection of the relevant coupling constants in the ^{1}H NMR spectra and verified by NOESY experiments, while the structure elucidation of **49** required more extensive NMR investigation (NOESY, COSY, HETCOR and long-range HETCOR). As is evident from the above results, the anion-stabilizing group has an effect on the stereochemical outcome in the aza-[2,3]-Wittig rearrangement of vinylaziridines, ranging from a complete *cis*-2,6-selectivity for the *tert*-butyl ester **17** to a modest *trans* selectivity for the anion derived from the propargyl derivative **26**. These experiments also seem to indicate that the mechanistic details of this reaction might not be as clear-cut as originally believed, since the formation of 1-pyrroline **49** is clearly not the result of a sigmatropic process (*vide infra*).[8] Finally, we have also investigated the potential of the benzyl derivative **23** and the unsaturated ester **31** as substrates for the rearrangement. However, subjecting **23** to a variety of bases (BuLi, *s*-BuLi, *t*-BuLi) gave only recovered starting material. The reason for this was a facile *ortho* lithiation of the aromatic nuclei, as shown by a D_2O quench.[39] Similarly, the enolate derived from **31** (LDA, KHMDS) also failed to react, perhaps due to the increased thermodynamic stability of the conjugated enolate.

Since it had been shown that a *tert*-butyl acetate moiety is the most efficient activating group for the

(35) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.17 (dd, 1H, J = 11.2, 2.8, C*H*CO_2^{t}Bu), 2.16 (dd, 1H, J = 11.0, 2.2, ^{t}BuC*H*).

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(37) Nakai, T.; Mikami, K.; Taya, S.; Fujita, Y. *J. Am. Chem. Soc.* **1981**, *103*, 6492−6494. Mikami, K.; Kimura, Y.; Kishi, N.; Nakai, T. *J. Org. Chem.* **1983**, *48*, 279−281.
(38) For a discussion of nitrogen-stabilized carbanions, see: Gawley, R. E.; Rein, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 3, Chapter 1.2.
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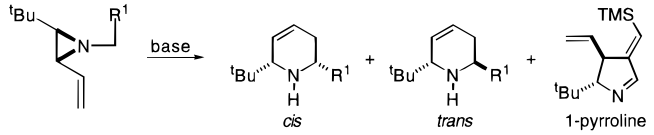
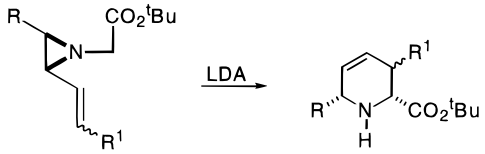
Table 1. The Influence of the Anion-Stabilizing Group on the [2,3]-Rearrangement



substrate	base[a]	products: cis	products: trans	products: pyrroline	ratio[b]	yield,[c] (%)
17, $R^1 = CO_2{}^tBu$	LDA	44	–	–	*cis* only	95
24, $R^1 = CN$	KHMDS	45	46	–	6.6:1	80
25, $R^1 = C{\equiv}CH$	d	–	–	–	–	0[e]
26, $R^1 = C{\equiv}CTMS$	*s*-BuLi	47	48	49	1.2:1.8:1	95
23, $R^1 = Ph$	d	–	–	–	–	0[e]
31, $R^1 = (E)$-$CHCHCO_2Me$	d	–	–	–	–	0[e]

[a] All reactions were run in THF at −78 °C. [b] Determined from ^1H NMR. [c] Combined crude yields. [d] −78 °C to rt. A variety of bases were tested, see text. [e] The starting material was recovered.

Scheme 3

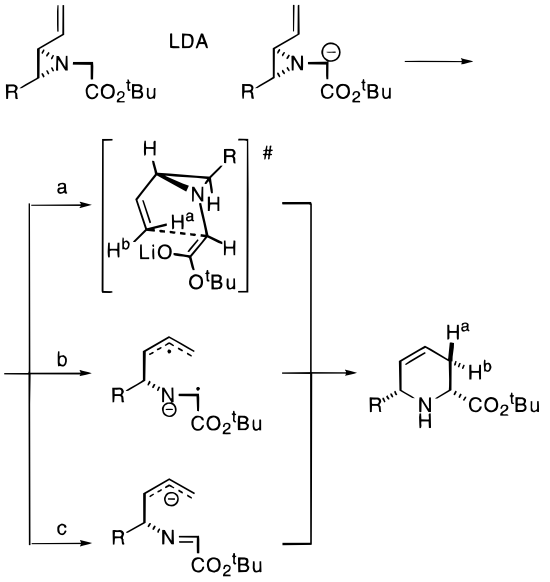


Substrate	Product	Yield
17	**44** R=^{t}Bu, R^1=H	95%
18	**50** R=^{t}Bu, R^1=β-Me	94%
19	**51** R=^{t}Bu, R^1=α-Me	92%
32	**52** R=$BnOCH_2$, R^1=H	98%
33	**53** R=$BnOCH_2$, R^1=β-Me	95%
34	**54** R=$BnOCH_2$, R^1=α-Me	94%
35	**55** R=C_6H_{13}, R^1=H	98%
36	**56** R=C_5H_{11}, R^1=β-Me	97%

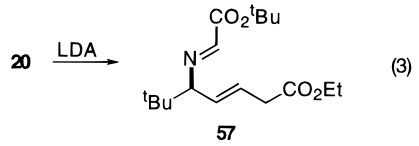
present rearrangement, we next decided to study the influence of the other ring substituents on the reaction outcome. As shown in Scheme 3, the results were gratifying, with the tetrahydropyridines being formed in excellent yields and, in each case, as a single diastereomer (Scheme 3). That the high selectivity observed in these rearrangements is the result of a kinetic formation of the *cis*-2,6-tetrahydropyridines and not due to a base-promoted equilibration of an initially formed mixture was shown by subjecting a mixture of racemic *cis*- and *trans*-tetrahydropyridines **52** and **58** (1.8:1) to the reaction conditions followed by standard isolation to yield the starting material with an unaffected isomeric ratio. Of particular interest is the complete selectivity observed in the rearrangements of the more highly substituted vinylaziridines **18**, **19**, **33**, **34**, and **36**. Apparently the stereochemical information supplied by the olefin is retained throughout the reaction, resulting in the formation of *trans*,*trans*-2,3,6-trisubstituted tetrahydropyridines **50**, **53**, and **56** when starting from (*Z*)-alkenes **18**, **33**, and **36**, respectively. Similarly, the (*E*)-substrates **19** and **34** upon treatment with LDA are transformed into the corresponding *cis*,*cis*-2,3,6-trisubstituted derivatives **51** and **54** with equally impressive selectivity.[40] Normally such high selectivity in these types of rearrangement is associated with a concerted reaction pathway in which the relative stereochemistry of the substrate, for stereoelectronic or steric reasons, is effectively communicated to the product. An indication that the present rearrangement might proceed by a more complicated,

(40) The *E*:*Z* ratio in the starting material is, in each case, retained as a 2,3-*cis*:*trans* ratio in the product.

Scheme 4



stepwise, mechanism was obtained when attempting to rearrange the unsaturated ester **20** (eq 3). When **20** was



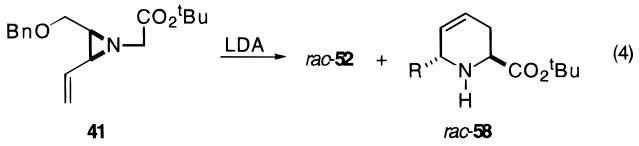
(3)

subjected to LDA (THF, −78 °C), the *β*,*γ*-unsaturated ester **57** was formed in high yield and as a single isomer, although the relative stereochemistry of the imine moiety has not yet been assigned with certainty. Apparently the enolate derived from **20** opens the three-membered ring to form a new enolate, which can be quenched with D_2O to yielded the α-deuterated *β*,*γ*-unsaturated ester with complete incorporation of deuterium. Also, attempts to rearrange silyl ether **22** gave a complicated mixture of products containing none of the expected tetrahydropyridine.

We believe that three different mechanisms are most likely for the [2,3]-rearrangements described above (Scheme 3). In the first of these, a concerted process which has also been invoked in the analogous rearrangements of allyl ethers,[1,2] there is a requirement for the enolate to be *cis* to the vinyl moiety so as to allow for efficient orbital overlap during C-C bond formation and opening of the three-membered ring (Scheme 4, path a). Such a mechanism correctly accounts for the stereochem-

ical outcome in the rearrangements of **17**−**19** and **32**−**36**. Alternatively, the enolate anion might disproportionate into a diradical anion followed by an intramolecular recombination to give the observed products (path b). Analogous mechanistic schemes have been proposed for the [1,2]-Wittig rearrangement of allylic ethers[1a,b] and have also been invoked in the rearrangement of certain allylic amines.[4b−d,6] Finally, a scenario in which the initially formed anion opens the ring to form an allylic anion which then makes a nucleophilic attack on the imine moiety can also be envisioned (path c). If the second or third mechanistic alternatives are indeed operating, involving discrete intermediates, the origin of the observed selectivities seems less obvious to rationalize.

In an effort to differentiate between these mechanistic possibilities and, hopefully, to provide some information about the origin of the stereoselectivity in the rearrangements, the following experiments were done. If a concerted mechanism is operating, vinylaziridines **41**−**43**, which exist as single *N*-invertomers with the ester moiety *trans* to the vinyl group, should afford products with different relative stereochemistry compared to the tetrahydropyridines obtained from **32**−**34**. Accordingly, rearrangement of **41** under standard conditions (LDA, THF, −78 °C) gave a mixture of *rac*-**52** and *rac*-**58** (1.8:1) in 93% yield (eq 4). In this reaction the *trans*-2,6-

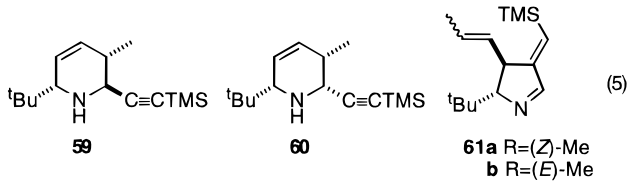


(4)

disubstituted derivative *rac*-**58** could conceivably be formed by a concerted pathway (cf. Scheme 3, path a), but formation of *rac*-**52** must involve a ring-opened intermediate. Even more surprising, however, was the finding that the (*Z*)-derivative **42** rearranged into *rac*-**53** (98%) as a single isomer while the (*E*)-derivative **43** under the same conditions gave *rac*-**54** (93%) as the sole product, neither of which would have been predicted to be the result of a concerted process. In addition, since vinylaziridines **33** and **42** both afford tetrahydropyridine **53** upon rearrangement while **34** and **43** give **54**, it seems reasonable to assume that these rearrangements occur via a common ring-opened intermediate for each pair of substrates.

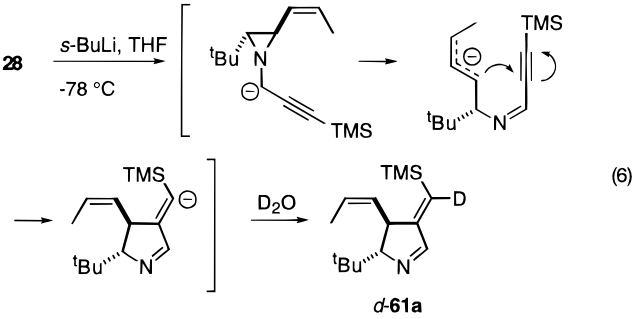
Since it has been shown that cleavage−diradical combination processes become more important at higher temperatures,[6] the rearrangement of **41** was reapeated at 0 °C and room temperature, but no change in yield or isomeric composition was observed. Identical results were also obtained when **41** was rearranged in the presence of *m*-dinitrobenzene, a radical trap.[41]

Finally, some evidence for the involvement of the allylic anion type of intermediate has been collected (Scheme 4, path c). As discussed previously, subjecting vinylaziridine **20** to LDA evidently produces such an intermediate, as was shown by a D_2O-quench. Furthermore, rearrangement of the propargyl derivative **28** (*s*-BuLi, −78 °C, THF) gives 1-pyrroline **61a** as the only isolated product in 98% yield while isomer **30** (*E*:*Z* 6:1) gave tetrahydropyridines **59** and **60** together with 1-pyrrolines **61a** and **61b** (**59**:**60**:**61a**:**61b** 4.9:2.4:1.4:1) in 49% combined isolated yield (eq 5).



(5)

The formation of 1-pyrrolines in these rearrangements is surprising. Some information about their mode of formation was obtained by repeating the experiment with aziridine **28** (*s*-BuLi, −78 °C, THF) and quenching the reaction with D_2O. This yielded *d*-**61a** as a single diastereomer with complete deuterium incorporation which suggests a mechanism in which the initially formed propargylic anion opens the aziridine ring to form the corresponding allylic anion (eq 6). Intramolecular addition of this anion to the alkyne moiety then gives a



(6)

vinylic anion, species known to be configurationally stable,[42] which is then quenched by D_2O to give *d*-**61a**, thus accounting for the exclusive formation of an (*E*)-vinylsilane in this process. No conclusive rationale for the mechanism of the [2,3]-rearrangement in vinylaziridines or the observed selectivities can be obtained from these experiments. However, it is clear that the mechanism is more complex than we originally suggested and that it might involve ring-opened intermediates and concurrent reaction pathways. Further studies to clarify these points are underway.

In conclusion, we have shown that various *N*-alkylated vinylaziridines can be prepared from the corresponding epoxy alcohols in reasonable overall yields. As for their [2,3]-rearrangement, *trans*-2,3-trisubstituted vinylaziridines having a *tert*-butyl ester moiety as an anion-stabilizing group rearrange with complete selectivity into the corresponding *cis*-2,6-disubstituted tetrahydropyridines. It has also been shown that (*Z*)-propenylaziridines afford *trans*,*trans*-2,3,6-trisubstituted tetrahydropyridines upon rearrangement, while (*E*)-propenylaziridines give the *cis*,*cis*-2,3,6-trisubstituted heterocycles with equally impressive selectivity. Other anion-stabilizing groups, such as a nitrile or an alkyne, perform less well in this reaction and give mixtures of products, while a phenyl and an α,β-unsaturated ester moiety apparently resist rearrangement. Finally, the mechanism of this reaction has been probed to some extent and it seems to be more complicated than originally assumed.

Experimental Section[43]

(2*S*,3*R*)-3-*tert*-Butyl-2-[[(*tert*-butyldimethylsilyl)oxy]-methyl]aziridine (3). A solution of (2*R*,3*S*)-2-azido-4,4-dimethyl-1,3-pentanediol[24] (457 mg, 2.64 mmol), *tert*-butyldi-

(41) Gong, J.; Fuchs, P. L. *J. Am. Chem. Soc.* **1996**, *118*, 4486−4487.

(42) Jenkins, P. R.; Symons, M. C. R.; Booth, S. E.; Swain, C. J. *Tetrahedron Lett.* **1992**, *33*, 3543.

(43) For general experimentals, see ref. 9.

methylsilyl chloride (478 mg, 3.18 mmol), triethylamine (0.58 mL, 3.70 mmol), and *N*,*N*-dimethyl-4-aminopyridine (cat.) in dry CH_2Cl_2 (20 mL) was stirred for 10 h at rt. The mixture was then poured into water (20 mL), and the organic phase was separated and washed with sat. NH_4Cl (10 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 15:1) gave (2*R*,3*S*)-4-azido-2,2-dimethyl-5-[(*tert*-butyldimethylsilyl)oxy]-3-pentanol (489 mg) in 64% overall yield from epoxide **1**. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.00 (m, 2H), 3.47 (dd, 1H, J = 5.6, 5.0), 3.29 (m, 1H), 2.89 (d, 1H, J = 4.9), 1.04 (s, 1H), 0.99 (s, 9H), 0.92 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 79.8, 65.1, 62.7, 34.9, 26.2, 25.9, 18.2, −5.5, −5.6; IR (neat) 3470, 2950, 2100 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{13}H_{30}N_3OSi$ (M + H): 288.2107, found: 288.2118.

A solution of the azido alcohol from above (427 mg, 1.49 mmol) and triphenylphosphine (468 mg, 1.78 mmol) in toluene (20 mL) was heated under reflux for 14 h. After cooling to rt the mixture was concentrated, and the residue was flash chromatographed (heptane:EtOAc 6:1 → 1:1) to give aziridine **3** (344 mg, 94%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.69 (m, 2H), 1.91 (m, 1H), 1.67 (d, 1H, J = 3.3), 0.88 (s, 9H), 0.88 (s, 9H), 0.44 (br s, 1H), 0.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 34.4, 30.0, 26.8, 25.8, 18.3, −5.3, −5.4; IR (neat) 3260, 2950 cm^{-1}; $[\alpha]^{20}_D$ +19.1 (*c* 2.63, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{13}H_{39}NOSi$ (M + H): 244.2097, found: 244.2101.

(2*S*,3*R*)-3-*tert*-Butyl-2-(hydroxymethyl)aziridine (4). To a solution of **3** (520 mg, 2.13 mmol) in THF (25 mL) at 0 °C was added tetrabutylammonium fluoride trihydrate (1.01 g, 3.20 mmol). The resultant mixture was stirred for 30 min at 0 °C. Concentration and flash chromatography (EtOAc:MeOH 1:0 → 4:1) of the residue yielded **4** (260 mg, 96%) as white crystals (mp 77−79 °C). ^{1}H NMR ($CDCl_3$,400 MHz) δ 3.83 (dd, 1H, J = 11.8, 3.3), 3.37 (dd, 1H, J = 11.8, 6.3), 2.63 (br s, 2H), 2.10 (m, 1H), 1.78 (br s, 1H), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 63.9, 45.2, 35.4, 30.4, 27.2; IR (neat) 3260, 2960, 1470, 1365 cm^{-1}; $[\alpha]^{22}_D$ = +22.3 (*c* 2.00, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_7H_{16}NO$ (M + H): 130.1232, found: 130.1231.

(2*S*,3*R*)-3-[(Benzyloxy)methyl]-2-[[(*tert*-butyldimethylsilyl)oxy]methyl]aziridine (5). Silylation of a mixture of (2*R*,3*S*)-2-azido-4-(benzyloxy)-1,3-butanediol and (2*S*,3*R*)-3-azido-4-(benzyloxy)-1,2-butanediol[24] as detailed for **3** gave after flash chromatography (heptane:EtOAc 10:1 → 4:1) (2*S*,3*R*)-3-azido-1-(benzyloxy)-4-[(*tert*-butyldimethylsilyl)oxy]-2-butanol and (2*S*,3*R*)-3-azido-4-(benzyloxy)-1-[(*tert*-butyldimethylsilyl)-oxy]-2-butanol as an inseparable mixture in 90% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks assigned from a mixture of regioisomers) δ 7.39−7.30 (m, 5H$_{maj}$, 5H$_{min}$), 4.61 (s, 2H$_{min}$), 4.59 (s, 2H$_{maj}$), 3.99 (dd, J = 10.7, 3.6, 1H$_{maj}$), 3.89 (dd, 1H$_{min}$, J = 10.0, 2.6), 3.86 (dd, 1H$_{maj}$, J = 10.6, 5.7), 3.82−3.77 (m, 1H$_{min}$), 3.75−3.66 (m, 1H$_{maj}$, 2H$_{min}$), 3.65−3.59 (m, 2H$_{min}$, 2H$_{maj}$), 3.53−3.48 (m, 1H$_{maj}$), 2.67 (d, 1H$_{maj}$, J = 5.5), 2.61 (d, 1H$_{min}$, J = 6.1), 0.93 (s, 9H$_{maj}$), 0.92 (s, 9H$_{min}$), 0.11 (s, 6H$_{maj}$), 0.10 (s, 6H$_{min}$); ^{13}C NMR ($CDCl_3$, 100 MHz, from a mixture of regioisomers) δ 138.2, 138.1, 128.9, 128.9, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 74.0, 74.0, 71.5, 71.3, 70.9, 70.4, 64.3, 64.1, 64.0, 62.5, 26.3, 26.2, 18.7, 18.6, −5.0, −5.1; IR (neat, from a mixture of regioisomers) 3450, 2920, 2090 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{17}H_{30}N_3O_3Si$ (M + H): 352.2056, found: 352.2062.

Aziridine 5. Flash chromatography (heptane:EtOAc 10:1 → 2:1) gave aziridine **5** in 88% yield as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37−7.29 (m, 5H), 4.57 (AB-q, 2H, J = 11.9, 7.2), 3.78 (d, 2H, J = 3.1), 3.59 (dd, 1H, J = 21.5, 4.6), 3.45 (dd, 1H, J = 10.5, 6.1), 2.17 (br s, 1H), 1.98 (d, 1H, J = 2.8), 0.89 (s, 9H), 0.74 (br s, 1H), 0.06 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.6, 128.8, 128.8, 128.2, 128.1, 128.1, 73.5, 36.0, 26.3, 18.7, −4.9, −5.0; IR (neat) 3280, 2920 cm^{-1}; $[\alpha]^{22}_D$ +22.3 (*c* 2.00, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{17}H_{30}NO_2Si$ (M + H): 308.2046, found: 308.2047.

***tert*-Butyl (2(2*S*,3*R*))-2-[3-*tert*-Butyl-2-[[((*tert*-butyldimethylsilyl)oxy]methyl]aziridin-1-yl]acetate (6).** Aziridine **3** (334 mg, 1.37 mmol), *tert*-butyl bromoacetate (0.333 mL, 2.06 mmol), K_2CO_3 (209 mg, 1.51 mmol), and 18-crown-6 (cat.) in THF (10 mL) were stirred for 4 days at rt. The white slurry was poured into Et_2O (30 mL) and washed with water (20 mL) and with brine (20 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 10:1 → 6:1) gave **6** (542 mg, 92%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.89 (dd, 1H, J = 11.8, 3.3), 3.75, (dd, 1H, J = 11.8, 6.7) 3.51 (d, 1H, J = 16.2), 3.07 (d, 1H, J = 16.2), 2.13 (dt, 1H, J = 6.8, 3.4), 1.46 (s, 9H), 1.39 (d, 1H, J = 3.4), 0.88 (s, 9H), 0.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.7, 80.7, 59.8, 55.3, 53.2, 39.4, 30.2, 28.1, 27.0, 25.8, 18.1, −5.4, −5.5; IR (neat) 2970, 1750 cm^{-1}; $[\alpha]^{20}_D$ −6.6 (*c* 2.28, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{19}H_{40}NO_3Si$ (M + H): 358.2775, found: 358.2800.

(2*S*,3*R*)-*N*-Benzyl-3-*tert*-butyl-2-[[(*tert*-butyldimethylsilyl)oxy]methyl]aziridine (7). A slurry of aziridine **3** (500 mg, 2.06 mmol), benzyl bromide (0.345 mL, 3.08 mmol), K_2CO_3 (312 mg, 2.26 mmol), and 18-crown-6 (cat.) in THF (15 mL) was stirred for 3 days at rt. The white slurry was poured into Et_2O (30 mL) and washed with water (20 mL) and brine (20 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 15:1 → 6:1) gave aziridine **7** (491 mg, 71%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.42−7.20 (m, 5H), 4.06 (d, 1H, J = 13.2), 3.98 (dd, 1H, J = 11.7, 3.6), 3.85, (dd, 1H, J = 11.7, 7.5) 3.55 (d, 1H, J = 13.2), 2.13 (dt, 1H, J = 7.5, 3.6), 1.39 (d, 1H, J = 3.6), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.5, 128.6, 128.1, 126.7, 60.0, 56.1, 52.9, 40.5, 30.1, 27.0, 25.9, 18.2, −5.3, −5.4; IR (neat) 2950, 1460 cm^{-1}; $[\alpha]^{20}_D$ +51.6 (*c* 3.05, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{20}H_{36}NOSi$ (M + H): 334.2566, found: 334.2562.

(2(2*S*,3*R*))-2-[3-*tert*-Butyl-2-[[(*tert*-butyldimethylsilyl)-oxy]methyl]aziridin-1-yl]acetonitrile (8). A slurry of aziridine **3** (1.40 g, 5.76 mmol), bromoacetonitrile (0.601 mL, 8.64 mmol), K_2CO_3 (875 mg, 6.30 mmol), and 18-crown-6 (cat.) in THF (20 mL) was stirred for 2 days at rt. The white slurry was then poured into Et_2O (50 mL) and washed twice with water (20 mL) and once with brine (20 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 9:1 → 4:1) gave the aziridine **8** (1.35 g, 92%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.05 (dd, 1H, J = 12.4, 2.6), 3.80, (dd, 1H, J = 12.4, 6.8) 3.70 (d, 1H, J = 16.6), 3.45 (d, 1H, J = 16.6), 2.20 (ddd, 1H, J = 6.8, 3.7, 2.6), 1.60 (d, 1H, J = 3.7), 0.88 (s, 9H), 0.10 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 118.4, 59.7, 52.8, 41.0, 40.1, 30.6, 27.2, 26.2, 18.6, −5.0, −5.1; IR (neat) 2960, 1470 cm^{-1}; $[\alpha]^{23}_D$ −1.4 (*c* 0.99, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{15}H_{30}N_2O$ (M + H): 283.2206, found: 283.2206.

(2*S*,3*R*)-3-*tert*-Butyl-2-[[(*tert*-butyldimethylsilyl)oxy]-methyl]-1-(2-propynyl)aziridine (9). To a solution of aziridine **3** (800 mg, 3.30 mmol) in THF (20 mL) were added K_2CO_3 (500 mg, 3.61 mmol), propargyl bromide (2.88 mL, 4.95 mmol, 80 wt % in toluene), and 18-crown-6 (cat.). The resultant slurry was stirred for 2.5 days at rt. The reaction mixture was then poured into Et_2O (50 mL) and washed with water (20 mL) and brine (20 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 50:1 → 8:1) gave **9** (852 mg, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.96 (dd, 1H, J = 11.9, 3.5), 3.78 (dd, 1H, J = 11.9, 7.1), 3.54 (dd, 1H, J = 16.6, 2.6), 3.25 (dd, 1H, J = 16.6, 2.6), 2.22 (t, 1H, J = 2.6), 2.14 (dt, 1H, J = 7.2, 3.6), 1.45 (d, 1H, J = 3.6) 1.89 (s, 9H), 1.87 (s, 9H), 0.08 (s, 6H); ^{13}C ($CDCl_3$, 75 MHz) δ 82.0, 71.5, 59.7, 52.7, 41.0, 40.4, 30.0, 27.0, 25.8, 18.2, −5.4, −5.5; IR (neat): 3280, 2940, 2195 cm^{-1}; $[\alpha]^{24}_D$ +9.9 (*c* 1.25, $CHCl_3$); HRMS(CI+). Exact mass calcd for $C_{16}H_{32}NOSi$ (M + H): 278.2253, found: 278.2253.

***tert*-Butyl (2(2*S*,3*R*))-2-[3-[(Benzyloxy)methyl]-2-[[(*tert*-butyldimethylsilyl)oxy]methyl]aziridin-1-yl]acetate (10).** To a solution of aziridine **5** (596 mg, 1.94 mmol) in THF (10 mL) was added 18-crown-6 (cat.), K_2CO_3 (295 mg, 2.13 mmol), and *tert*-butyl bromoacetate (470 μL, 2.91 mmol). The resultant slurry was stirred at rt for 72 h. The reaction mixture was poured into water (20 mL), and the organic layer was separated. The aqueous phase was washed with Et_2O (4 × 15 mL), and the combined organic layers were washed with brine (15 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 8:1 → 1:1) gave **10** (436 mg, 53%). ^{1}H NMR ($CDCl_3$, 400 MHz, peaks assigned from a mixture of invertomers) δ 7.38−7.28 (m, 5H$_{maj}$, 5H$_{min}$), 4.58 (AB-q, 2H$_{maj}$, J = 12.0, 9.0), 4.55 (AB-q, 2H$_{min}$, J = 12.0, 5.8), 4.01−3.95 (m, 1H$_{maj}$, 1H$_{min}$), 3.87−3.78 (m, 1H$_{maj}$, 1H$_{min}$), 3.70−3.61 (m, 1H$_{maj}$, 1H$_{min}$), 3.53−3.41 (m, 2H$_{maj}$, 2H$_{min}$), 3.28 (d,

$1H_{maj}$, $J = 16.6$), 3.15 (d, $1H_{min}$, $J = 16.5$), 2.30−2.25 (m, $1H_{min}$), 2.21−2.16 (m, $1H_{maj}$), 1.99−1.94 (m, $1H_{maj}$), 1.84−1.79 (m, $1H_{min}$), 1.47 (s, $9H_{maj}$, $9H_{min}$), 0.90 (s, $9H_{maj}$, $9H_{min}$), 0.07 (s, $6H_{maj}$, $6H_{min}$); ^{13}C NMR ($CDCl_3$, 100 MHz, from a mixture of invertomers) δ 170.9, 170.6, 138.8, 138.3, 128.8, 128.8, 128.2, 128.1, 128.1, 128.0, 81.4, 81.3, 73.5, 73.1, 72.5, 66.5, 65.7, 59.4, 54.4, 54.1, 44.4, 41.8, 41.2, 40.2, 28.5, 26.4, 26.3, 18.8, 18.6, −4.8, −5.0; IR (neat, from a mixture of invertomers) 2850, 1720, 1245 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{23}H_{40}NO_4Si$ (M + H): 422.2727, found: 422.2734.

***tert*-Butyl (2(2*S*,3*R*))-2-[3-*tert*-Butyl-2-(hydroxymethyl)aziridin-1-yl]acetate (11).** To a solution of **6** (1.0 g, 2.79 mmol) in THF (20 mL) at 0 °C was added tetrabutylammonium fluoride (1.32 g, 4.18 mmol), and the resultant mixture was stirred for 30 min at 0 °C and then warmed to rt over 15 min. The reaction mixture was poured into Et_2O (30 mL) and washed once with water (30 mL) and once with brine (20 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 3:1 → 1:2) gave **11** (522 mg, 77%). ^1H NMR ($CDCl_3$, 300 MHz) δ 3.90 (ddd, 1H, $J = 13.0, 10.1, 2.7$), 3.64−3.44 (m, 3H), 3.04 (d, 1H, $J = 16.6$), 2.38 (dt, 1H, $J = 10.1, 3.0$), 1.48 (s, 9H), 1.12 (d, 1H, $J = 3.0$), 0.88 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.0, 82.2, 58.9, 54.4, 52.1, 41.3, 30.4, 28.0, 26.9; IR (neat) 3420, 2960, 1745 cm^{-1}; $[\alpha]^{22}_D$ −52.4 (*c* 5.28, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{13}H_{26}NO_3$ (M + H): 244.1912, found: 244.1911.

(2*S*,3*R*)-*N*-Benzyl-3-*tert*-butyl-2-(hydroxymethyl)aziridine (12). Prepared from **7** in 92% yield as detailed for **11**. Flash chromatography (heptane:EtOAc 6:1 → 1:1) furnished **12** as a white solid (mp 89−91 °C). ^1H NMR ($CDCl_3$, 300 MHz) δ 7.48−7.20 (m, 5H), 4.02−3.88 (m, 2H), 3.78 (dd, 1H, $J = 12.2, 8.7$), 3.49 (m, 1H), 2.82 (br s, 1H), 2.24 (dt, 1H, $J = 8.7, 3.6$), 1.36 (d, 1H, $J = 3.6$), 0.78 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.0, 128.4, 128.3, 127.0, 59.8, 56.3, 53.6, 40.4, 30.3, 26.9; IR (KBr) 3450, 2960 cm^{-1}; $[\alpha]^{22}_D$ +52.4 (*c* 1.47, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{14}H_{22}NO$ (M + H): 220.1701, found: 220.1705.

(2(2*S*,3*R*))-2-[3-*tert*-Butyl-2-(hydroxymethyl)aziridin-1-yl]acetonitrile (13). Prepared from **8** in 89% yield as detailed for **11**. Flash chromatography (heptane:EtOAc 1:1 → 1:5) gave **13** as an oil. ^1H NMR ($CDCl_3$, 300 MHz) δ 4.06 (dd, 1H, $J = 12.9, 2.7$), 3.76 (dd, 1H, $J = 12.9, 7.9$), 3.72 (d, 1H, $J = 16.7$), 3.44 (d, 1H, $J = 16.7$), 2.32 (br s 1H), 2.24 (m, 1H), 1.54 (d, 1H, $J = 3.9$), 0.90 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 117.9, 58.9, 53.2, 40.5, 39.8, 30.2, 26.7; IR (neat) 3360, 2950, 2250 cm^{-1}; $[\alpha]^{24}_D$ +13.1 (*c* 2.15, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_9H_{17}N_2O$ (M + H): 169.1341, found: 169.1350.

(2*S*,3*R*)-3-*tert*-Butyl-2-(hydroxymethyl)-1-(2-propynyl)aziridine (14). Prepared from **9** in 92% yield as detailed for **11**. Flash chromatography (heptane:EtOAc 6:1 → 1:3) gave **14** as a white solid (mp 93 °C). ^1H NMR ($CDCl_3$, 300 MHz) δ 3.96 (dd, 1H, $J = 12.9, 3.2$), 3.74 (dd, 1H, $J = 12.9, 9.0$), 3.52 (dd, 1H, $J = 16.7, 2.5$), 3.27 (dd, 1H, $J = 16.7, 2.5$), 2.34 (t, 1H, $J = 2.6$), 2.26 (dt, 1H, $J = 9.0, 3.6$), 2.11 (br s, 1H), 1.31(d, 1H, $J = 3.9$) 1.89(s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 81.6, 72.4, 59.5, 53.9, 41.3, 40.6, 30.2, 26.9; IR (KBr) 3180, 2940, 2130 cm^{-1}; $[\alpha]^{24}_D$ −35.9 (*c* 1.45, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{10}H_{18}NO$ (M + H): 168.1384, found: 168.1387.

Methyl (4(2*S*,3*R*))-4-[3-*tert*-Butyl-2-(hydroxymethyl)-aziridin-1-yl]-2-(*E*)-butenoate (15). To a solution of **4** (170 mg, 1.31 mmol) in THF (20 mL) were added 18-crown-6 (cat.), K_2CO_3 (200 mg, 1.45 mmol), and methyl *trans*-4-bromo-2-butenoate (236 μL, 1.97 mmol). The resultant slurry was stirred at rt for 40 h and then diluted with Et_2O (50 mL). The combined organic phases were washed with water (30 mL). The aqueous phase was washed with Et_2O (4 × 15 mL), and the combined organic layers were washed with brine (15 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 1:10 → 0:1) gave **15** (248 mg, 83%) as an off-white solid (mp 59−63 °C). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.06 (dt, 1H, $J = 15.7, 5.3$), 6.12 (dt, 1H, $J = 15.7, 1.6$), 3.92 (dd, 1H, $J = 12.3, 3.1$), 3.75−3.68 (m, 4H), 3.50 (ddd, 1H, $J = 16.6, 4.9, 1.9$), 3.19 (dd, 1H, $J = 16.6, 5.6$), 2.11 (br s, 1H), 1.27 (d, 1H, $J = 3.6$), 0.87 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.4, 147.2, 121.8, 59.9, 54.1, 53.6, 52.0, 40.5, 30.7, 27.4; IR (neat) 3190, 2960, 1720 cm^{-1}; $[\alpha]^{22}_D$ +18.2 (*c* 2.00, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{12}H_{22}NO_3$ (M + H): 228.1600, found: 228.1600.

***tert*-Butyl (2(2*S*,3*R*))-2-[3-[(benzyloxy)methyl]-2-(hydroxymethyl)aziridin-1-yl]acetate (16).** Prepared from **10** in 91% yield as detailed for **11**. Flash chromatography (heptane:EtOAc 1:2 → 1:10) gave alcohol **16** as an oil. ^1H NMR ($CDCl_3$, 400 MHz, peaks assigned from a mixture of invertomers) δ 7.39−7.28 (m, $5H_{maj}$, $5H_{min}$), 4.58−4.50 (m, $2H_{maj}$, $2H_{min}$), 3.97−3.89 (m, $1H_{maj}$, $1H_{min}$), 3.84−3.75 (m, $1H_{min}$), 3.72−3.43 (m, $3H_{maj}$, $3H_{min}$), 3.29−3.22 (m, $1H_{maj}$), 3.12−3.05 (m, $1H_{min}$), 2.93 (d, $1H_{maj}$, $J = 17.1$), 2.41−2.28 (m, $1H_{maj}$, $1H_{min}$), 1.95−1.80 (m, $1H_{maj}$, $1H_{min}$), 1.69 (br s, $1H_{maj}$, $1H_{min}$), 1.48 (s, $9H_{maj}$, $9H_{min}$); ^{13}C NMR ($CDCl_3$, 100 MHz, from a mixture of invertomers) δ 172.0, 168.5, 138.1, 128.9, 128.3, 128.2, 128.2, 128.1, 82.4, 73.8, 73.5, 73.4, 70.4, 66.5, 64.8, 63.4, 53.3, 51.2, 45.0, 39.2, 36.4, 33.7, 28.5; IR (neat, from a mixture of invertomers) 3420, 2920, 1730 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{17}H_{26}NO_4$ (M + H): 308.1862, found: 308.1860.

***tert*-Butyl (2(2*R*,3*R*))-2-(3-*tert*-Butyl-2-vinylaziridin-1-yl)acetate (17).** To a stirred solution of DMSO (114 μL, 1.61 mmol) in CH_2Cl_2 (5 mL) at −78 °C was added oxalyl chloride (56.3 μL, 0.664 mmol), and stirring was continued for 5 min. Alcohol **11** (78.3 mg, 0.322 mmol) in CH_2Cl_2 (5 mL) was added *via* cannula to the mixture, and stirring was continued for 30 min at −78 °C. Triethylamine (0.538 mL, 3.86 mmol) was then added, and the mixture was slowly warmed to rt over 2 h. The mixture was then poured into Et_2O (20 mL) and washed twice with water (2 × 20 mL) and once with brine (20 mL). Drying ($MgSO_4$) and concentration furnished the crude aldehyde which was taken on to the next step without further purification.

To a solution of methyltriphenylphosphonium bromide (367 mg, 0.998 mmol) in toluene (5 mL) at −15 °C was added KHMDS (0.460 mL, 0.966 mmol, 2.1 M in THF), and the resultant yellow slurry was stirred for 30 min at −15 °C to rt and then recooled to −15 °C. The crude aldehyde from above (0.322 mmol) in THF (10 mL) was then added *via* cannula, and stirring was continued for 20 min at −15 °C to rt. The yellow slurry was then poured into brine (10 mL), and the aqueous phase was extracted with Et_2O (3 × 10 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 10:1 → 3:1) furnished **17** (71.4 mg, 92%). ^1H NMR ($CDCl_3$, 300 MHz) δ 5.65 (m, 1H), 5.35 (dd, 1H, $J = 17.0, 1.8$), 5.23 (dd, 1H, $J = 10.1, 1.7$), 3.25 (d, 1H, $J = 16.2$), 3.07 (d, 1H, $J = 16.2$), 2.52 (dd, 1H, $J = 8.3, 3.4$), 1.44 (s, 9H), 1.43 (m, 1H), 0.90 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.1, 133.2, 120.3, 80.9, 57.8, 56.4, 40.8, 30.7, 28.1, 26.8; IR (neat) 2945, 1745 cm^{-1}; $[\alpha]^{20}_D$ +69.6 (*c* 4.19, CH_2Cl_2); HRMS (CI+). Exact mass calcd for $C_{14}H_{26}NO_2$ (M + H): 240.1964, found: 240.1984.

***tert*-Butyl (2(2*R*,3*R*))-2-[3-*tert*-Butyl-2-[(*Z*)-1-propenyl]-aziridin-1-yl]acetate (18).** The aldehyde was prepared from **11** as detailed for **17**. To a solution of ethyltriphenylphosphonium bromide (473 mg, 1.27 mmol) in toluene (5 mL) at −15 °C was added KHMDS (0.806 mL, 1.23 mmol, 1.5 M in THF), and the resultant yellow slurry was stirred for 30 min at −15 °C to rt and then recooled to −15 °C. The crude aldehyde from above (0.411 mmol) in THF (10 mL) was added *via* cannula, and stirring was continued for 20 min at −15 °C to rt. The yellow slurry was then poured into brine (10 mL), and the aqueous phase was extracted with Et_2O (3 × 10 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 10:1 → 3:1) gave **18** (54 mg, 52%) as an inseparable mixture of isomers (*E*:*Z* < 1:15). ^1H NMR ($CDCl_3$, 300 MHz) δ 5.75 (ddq, 1H, $J = 10.8, 7.0, 1.8$), 5.20 (m, 1H), 3.26 (d, 1H, $J = 16.1$), 3.02 (d, 1H, $J = 16.1$), 2.66 (ddd, 1H, $J = 9.0, 3.5, 1.0$), 1.77 (dd, 3H, $J = 7.0, 1.8$), 1.43 (s, 9H), 1.37 (d, 1H, $J = 3.6$), 0.90 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.3, 131.0, 124.8, 80.8, 59.1, 56.7, 35.2, 30.7, 28.1, 26.9, 13.3; IR (neat) 2950, 1745 cm^{-1}; $[\alpha]^{20}_D$ +110.9 (*c* 2.70, $CDCl_3$); HRMS (CI+). Exact mass calcd for $C_{15}H_{28}NO_2$ (M + H): 254.2120, found: 254.2118.

***tert*-Butyl (2(2*R*,3*R*))-2-[3-*tert*-Butyl-2-[(*E*)-1-propenyl]-aziridin-1-yl]acetate (19).** The aldehyde was prepared from **11** as detailed for **17**. To a stirred slurry of ethyltriphenylphosphonium bromide (549 mg, 1.47 mmol) in THF (6 mL) at 0 °C was added freshly prepared PhLi (1.48 mL, 1.47 mmol, 0.99 M in Et_2O), and the resultant deep-red solution was

stirred at 0 °C for 20 min. After cooling to −70 °C the aldehyde in Et_2O (6 mL) was added dropwise over 10 min. After stirring for 5 min at −70 °C the solution was warmed to −30 °C, and an additional portion of PhLi (1.48 mL, 1.47 mmol, 0.99 M in Et_2O) was added. The mixture was stirred at −30 °C for 5 min, and then dry MeOH (0.200 mL, 5 mmol) was added followed by phosphate buffer (2 mL, pH 7). The mixture was warmed to rt over 2 h and then poured into brine (20 mL), and the organic layer was separated. The aqueous phase was extracted with Et_2O (3 × 20 mL), and the combined organic phases were washed with brine (20 mL). Drying ($MgSO_4$), concentration and flash chromatography (heptane: EtOAc 10:1 → 4:1) gave **19** (27 mg, 8%) as a mixture of isomers (*E*:*Z* 3.5:1). ^{1}H NMR ($CDCl_3$, 300 MHz, peaks assigned from a mixture of isomers) δ 5.76 (m, 1H), 5.20 (ddq, 1H, J = 15.2, 8.4, 1.6), 3.23 (d, 1H, J = 16.1), 3.04 (d, 1H, J = 16.1), 2.49 (dd, 1H, J = 8.3, 3.6), 1.71 (dd, 3H, J = 6.4, 1.6), 1.43 (s, 9H); 1.39 (d, 1H, J = 3.6), 0.92 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, peaks assigned from a mixture of isomers) δ 170.3, 131.9, 125.8, 80.7, 57.8, 56.4, 40.1, 30.6, 28.1, 26.9, 18.1; IR (neat) 2950, 1750 cm^{-1}.

***tert*-Butyl (2(2*R*,3*R*))-2-[3-*tert*-Butyl-2-[(*E*)-2-(ethoxycarbonyl)vinyl]aziridin-1-yl]acetate (20).** To a stirred solution of DMSO (0.455 mL, 6.41 mmol) in CH_2Cl_2 (20 mL) at −78 °C was added oxalyl chloride (224 μL, 2.56 mmol), and stirring was continued for 5 min. Alcohol **11** (312 mg, 1.28 mmol) in CH_2Cl_2 (10 mL) was added *via* cannula and stirring was continued for 30 min at −78 °C. Triethylamine (2.13 mL, 15.3 mmol) was then added, and stirring was continued at −78 °C for 30 min before (carbethoxymethylene)triphenylphosphorane (1.79 g, 5.13 mmol) was added. Stirring was continued for 30 min at −78 °C, and the mixture was then slowly warmed to 0 °C over 30 min. The mixture was poured into brine (20 mL), and the aqueous phase was extracted with Et_2O (3 × 20 mL). Drying ($MgSO_4$), concentration, and flash chromatography (heptane:EtOAc 6:1 → 1:1) gave **20** (318 mg, 80%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.68 (dd, 1H, J = 15.4, 10.1), 6.10 (d, 1H, J = 15.4), 4.18 (q, 2H, J = 7.2), 3.35 (d, 1H, J = 16.1), 3.23 (d, 1H, J = 16.1), 2.63 (dd, 1H, J = 10.1, 3.2), 1.63 (d, 1H, J = 3.2), 1.44 (s, 9H), 1.27 (t, 3H, J = 7.2), 0.89 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.4, 165.7, 144.1, 124.7, 81.3, 60.4, 59.8, 56.8, 39.4, 31.1, 28.0, 26.8, 14.3; IR (neat) 2960, 1750, 1645 cm^{-1}; $[\alpha]^{22}_D$ +114.4 (*c* 2.67, $CDCl_3$); HRMS (CI+). Exact mass calcd for $C_{17}H_{30}NO_4$ (M + H): 321.2175, found: 312.2167.

***tert*-Butyl (2(2*R*,3*R*))-2-[3-*tert*-Butyl-2-[(*E*)-3-hydroxy-1-propenyl]-aziridin-1-yl]acetate (21b).** The aldehyde was prepared from **11** as detailed for **17**. To a solution of the aldehyde (2.07 mmol) from above in benzene (20 mL) at 0 °C was added (triphenylphosphoranylidene)acetaldehyde (3.15 g, 10.37 mmol), and the resultant mixture was stirred for 20 min at 0 °C and then at rt for 2 days. Filtration, concentration, and flash chromatography (heptane:EtOAc 3:1) gave **21a** (104 mg, 19%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.5 (d, 1H, J = 7.5), 6.57 (dd, 1H, J = 15.3, 9.6), 6.39 (dd, 1H, J = 15.3, 7.5), 3.34 (AB-q, 2H, J = 1.0), 2.75 (dd, 1H, J = 9.6, 3.1), 1.71 (d, 1H, J = 3.1), 1.45 (s, 9H), 0.96 (s, 9H).

Reduction of aldehyde **21a**. To a solution of the aldehyde **21a** (104 mg, 0.391 mmol) in EtOH (5 mL) at −40 °C was added $NaBH_4$ (7 mg, 0.391 mmol), and the resultant mixture was stirred for 20 min at −40 °C. The reaction was quenched by the addition of acetaldehyde (44 μL, 0.782 mmol), and the mixture was allowed to warm to rt. The mixture was then poured into Et_2O (20 mL) and washed with water (2 × 20 mL) and brine (20 mL). Drying ($MgSO_4$) and concentration gave **21b** (95 mg, 90%) ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.02 (dt 1H, J = 15.3, 5.1), 5.53 (ddt, 1H, J = 15.3, 8.8, 1.5), 4.14 (d, 2H, J = 5.1), 3.26 (d, 1H, J = 16.1), 3.05 (d, 1H, J = 16.1), 2.54 (dd, 1H,, J = 8.8 3.5), 1.84 (br s, 1H), 1.45 (s, 9H), 1.43 (d, 1H, J = 3.5), 0.90 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.1, 135.3, 126.4, 81.0, 63.0, 58.2, 56.5, 39.7, 30.3, 28.1, 26.8; IR (neat) 3360, 2950, 1735 cm^{-1}; $[\alpha]^{22}_D$ +74.0 (*c* 1.47, $CDCl_3$); HRMS (CI+). Exact mass calcd for $C_{15}H_{28}NO_2$ (M + H): 270.2069, found: 270.2073.

***tert*-Butyl (2(2*R*,3*R*))-2-[3-*tert*-Butyl-2-((*E*)-3-[(*tert*-butyldiphenylsilyl)oxy]-1-propenyl)aziridin-1-yl]acetate (22).** A solution of alcohol **21b** (22 mg, 0.081 mmol), *tert*-butyldiphenylsilyl chloride (31 μL, 0.122 mmol), triethylamine (19 μL, 0.138 mmol), and *N*,*N*-dimethyl-4-aminopyridine (cat.) in CH_2Cl_2 (5 mL) was stirred for 7 h at rt. The mixture was then poured into Et_2O (10 mL) and washed with water (10mL) and brine (10 mL). The organic phase was dried ($MgSO_4$), concentrated, and and flash chromatographed (heptane:EtOAc 10:1 → 6:1) to furnish silyl ether **22** (41 mg, 99%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75−7.65 (m, 4H), 7.48−7.34 (m, 6H), 5.89 (dt 1H, J = 15.2, 4.6), 5.53 (ddt, 1H, J = 15.2, 8.6, 1.5), 4.22 (dd, 2H, J = 4.6, 1.5), 3.25 (d, 1H, J = 16.1), 3.01 (d, 1H, J = 16.1), 2.54 (dd, 1H, J = 8.6, 3.5), 1.48 (s, 9H), 1.40 (d, 1H, J = 3.5), 1.07 (s, 9H), 0.92 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.2, 135.5, 135.1, 134.8, 133.6, 129.7, 127.7, 124.8, 80.8, 64.0, 58.1, 56.4, 39.7, 30.7, 28.1, 26.9, 26.8, 26.5, 19.2; IR (neat) 2960, 1750 cm^{-1}; $[\alpha]^{20}_D$ +39.4 (*c* 1.55, $CDCl_3$); HRMS (CI+). Exact mass calcd for $C_{31}H_{46}NO_2Si$ (M + H): 508.3247, found: 508.3254.

(2*R*,3*R*)-*N*-Benzyl-3-*tert*-butyl-2-vinylaziridine (23). Prepared from alcohol **12** in 94% yield as detailed for vinylaziridine **17**. Flash chromatography (heptane:EtOAc 20:1) gave **23** as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.45−7.20 (m, 1H), 5.87 (ddd, 1H, J = 17.0, 10.2, 8.8), 5.41 (dd, 1H, J = 17.0, 1.7), 5.26 (dd, 1H, J = 10.2, 1.7), 3.90 (d, 1H, J = 13.2), 3.41 (d, 1H, J = 13.2), 2.57 (dd, 1H, J = 8.8, 3.4), 1.43 (d, 1H, J = 3.4), 0.80 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.3, 134.1, 128.5, 128.1, 126.8, 119.4, 57.5, 57.3, 41.9, 30.6, 26.9; IR (neat) 2950, 1660 cm^{-1}; $[\alpha]^{22}_D$ +151.2 (*c* 2.99, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{15}H_{22}N$ (M + H): 216.1752, found: 216.1762.

(2(2*R*,3*R*))-2-(3-*tert*-Butyl-2-vinylaziridin-1-yl)acetonitrile (24). Prepared from **13** in 40% yield as detailed for **17**. Flash chromatography (heptane:EtOAc 4:1) gave **24** as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.70 (ddd, 1H, J = 16.9, 10.1, 8.1), 5.46 (dd, 1H, J = 16.9, 1.5), 5.40 (dd, 1H, J = 10.1, 1.6), 3.49 (d, 1H, J = 16.6), 3.28 (d, 1H, J = 16.6), 2.58 (dd, 1H, J = 8.1, 3.7), 1.60 (d, 1H, J = 3.7), 0.90 (s, 9H,); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 131.2, 122.8, 177.4, 57.1, 41.8, 40.4, 30.6, 26.6; IR (neat) 2960, 2255, 1640; $[\alpha]^{22}_D$ +118.6 (*c* 1.51, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{10}H_{17}N_2$ (M + H): 165.1392, found: 165.1389.

(2*R*,3*R*)-3-*tert*-Butyl-1-(2-propynyl)-2-vinylaziridine (25). Prepared from **14** in 83% yield as detailed for **17**. Flash chromatography (heptane:EtOAc 20:1 → 6:1) gave **25** as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.76 (ddd, 1H, J = 17.0, 10.2, 8.5), 5.39 (dd, 1H, J = 17.0, 1.7), 5.28 (dd, 1H, J = 10.2, 1.7), 3.36 (dd, 1H, J = 16.5, 2.5), 3.19 (dd, 1H, J = 16.5, 2.4), 2.52 (dd, 1H, J = 8.5, 3.7), 2.25 (t, 1H, J = 2.5), 1.55 (d, 1H, J = 3.5), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 132.9, 120.4, 81.5, 71.9, 56.8, 41.9, 41.6, 30.5, 26.8; IR (neat) 3300, 2950 cm^{-1}; $[\alpha]^{22}_D$ +130.6 (*c* 1.61, $CDCl_3$); HRMS (CI+). Exact mass calcd for $C_{10}H_{18}N$ (M + H): 164.1439, found: 164.1437.

(2*R*,3*R*)-3-*tert*-Butyl-1-[3-(trimethylsilyl)-2-propynyl]-2-vinylaziridine (26). To a solution of **25** (349 mg, 2.13 mmol) in THF (20 mL) at −78 °C was added *n*-BuLi (2.31 mL, 3.04 mmol, 1.6M in hexanes), and stirring was continued for 30 min at −78 °C. TMSCl (0.406 mL, 3.04 mmol) was then added and after 1.5 h of stirring at −78 °C the reaction was quenched by addition of pH 7 buffer (2 mL). The resultant mixture was allowed to reach rt, poured into pH 7 buffer (10 mL), and extracted with Et_2O (2 × 20 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. Flash chromatography of the residue (heptane:EtOAc 10:1) gave **26** (432 mg, 86%). ^{1}H NMR($CDCl_3$, 300 MHz) δ 5.73 (ddd, 1H, J = 17.0, 10.2, 8.5), 5.37 (dd, 1H, J = 17.0, 1.7), 5.25 (dd, 1H, J = 10.2, 1.7), 3.43 (d, 1H, J = 16.6), 3.11 (d, 1H, J = 16.6), 2.50 (dd, 1H, J = 8.5, 3.7), 1.56 (d, 1H, J = 3.7), 0.91 (s, 9H), 0.14 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 133.1, 120.3, 88.6, 71.9, 56.7, 42.8, 41.8, 30.4, 26.9, −10.8; IR (neat) 2960, 2180, 1250, 1050 cm^{-1}; $[\alpha]^{24}_D$ +168.0 (*c* 1.39, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{14}H_{26}NSi$ (M + H): 236.1835, found: 236.1834.

(2*R*,3*R*)-3-*tert*-Butyl-2-[(*Z*)-1-propenyl]-1-(2-propynyl)-aziridine (27). Prepared from **14** in 81% yield as detailed for **18**. Flash chromatography (heptane:EtOAc 20:1 → 6:1) gave **27** as an inseparable mixture of isomers (*E*:*Z* 1:11). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.79 (ddq, 1H, J = 10.7, 7.0, 1.1), 5.30 (ddd, 1H, J = 10.7, 8.6, 1.6), 3.33 (dd, 1H, J = 16.6, 2.5), 3.13 (dd, 1H, J = 16.6, 2.5), 2.64 (dd, 1H, J = 8.6, 3.5), 2.23 (t, 1H, J = 2.5), 1.77 (dd, 3H, J = 7.0, 1.6), 1.45 (d, 1H, J = 3.5),

0.90 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 133.1, 124.4, 81.8, 58.0, 42.1, 36.1, 30.5, 26.9, 13.4; IR (neat) 3310, 2950, 2190 cm^{-1}; $[\alpha]^{24}_D$ +175.8 (*c* 0.609, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{12}H_{20}N$ (M + H): 178.1596, found: 178.1693.

(2*R*,3*R*)-3-*tert*-Butyl-1-[3-(trimethylsilyl)-2-propynyl]-2-((*Z*)-1-propenyl)aziridine (28). Prepared from **27** in 83% yield as detailed for **26**. Flash chromatography (heptane:EtOAc 20:1 → 10:1) gave **28** as an inseparable mixture of isomers (*E*:*Z* 1:11). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.77 (ddq, 1H, *J* = 10.8, 6.9, 1.1), 5.37 (ddq, 1H, *J* = 10.4, 8.5, 1.6), 3.38 (d, 1H, *J* = 16.6), 3.06 (d, 1H, *J* = 16.6), 2.62 (dd, 1H, *J* = 8.7, 3.8), 1.76 (dd, 3H, *J* = 7.0, 1.7), 1.76 (d, 1H, *J* = 3.7), 0.89 (s, 9H), 0.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 133.1, 124.5, 103.9, 88.3, 57.9, 43.1, 36.1, 30.4, 26.9, 13.4, −11.2; IR (neat) 2960, 2190 cm^{-1}; $[\alpha]^{24}_D$ +229.1 (*c* 1.63, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{14}H_{26}NSi$ (M + H): 250.1991, found: 250.1982.

(2*R*,3*R*)-3-*tert*-Butyl-2-[(*E*)-1-propenyl]-1-(2-propynyl)-aziridine (29). Prepared from alcohol **14** in 32% yield as detailed for vinylaziridine **19**. Flash chromatography (heptane:EtOAc 20:1 → 6:1) gave vinylaziridine **29** as an inseparable mixture isomers (*E*:*Z* 3.2:1). ^{1}H NMR($CDCl_3$, 300 MHz, peaks assigned from a mixture of isomers) δ 5.81 (m, 1H), 5.37 (m, 1H), 3.34 (dd, 1H, *J* = 16.6, 2.6), 3.06 (d, 1H, *J* = 16.6, 2.6), 2.57 (dd, 1H, *J* = 8.2, 3.7), 2.32 (m, 1H), 1.73 (dd, 3H, *J* = 6.6, 1.7), 1.47 (d, 1H, *J* = 3.6 Hz), 0.88 (s, 9H).

(2*R*,3*R*)-3-*tert*-Butyl-1-[3-(trimethylsilyl)-2-propynyl]-2-[(*E*)-1-propenyl]aziridine (30). Prepared from **29** in 70% yield as detailed for **26**. Flash chromatography (heptane:EtOAc 20:1 → 10:1) gave **30** as an inseparable mixture of isomers (*E*:*Z* 3.2:1). ^{1}H NMR ($CDCl_3$, 300 MHz, assigned from a mixture of isomers) δ 5.79 (m, 1H), 5.36 (dd, 1H, *J* = 16.8, 8.1), 3.40 (d, 1H, *J* = 16.6), 3.06 (d, 1H, *J* = 16.6), 2.46 (dd, 1H, *J* = 8.1, 3.6), 1.73 (dd, 3H, *J* = 6.6, 1.2), 1.49 (d, 1H, *J* = 3.6 Hz), 0.88 (s, 9H), 0.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, assigned from a mixture of isomers) δ 131.9, 125.6, 104.1, 88.3, 56.6, 42.7, 41.1, 30.3, 26.9, 18.1, −0.1; IR (neat) 2960, 2195, 1460, 1250 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{15}H_{28}NSi$ (M + H): 250.1991, found: 250.1979.

Methyl (4(2*R*,3*R*))-4-(3-*tert*-Butyl-2-vinylaziridin-1-yl)-(*E*)-2-butenoate (31). Prepared from alcohol **15** in 17% yield as detailed for vinylaziridine **17**. Flash chromatography (heptane:EtOAc 8:1 → 5:1) gave vinylaziridine **31** as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.00 (dt, 1H, *J* = 15.6, 5.2), 6.10 (dt , 1H, *J* = 15.7, 3.7), 5.75−5.64 (m, 1H), 5.38 (dd, 1H, *J* = 16.9, 1.2), 5.25 (dd, 1H, *J* = 10.2, 1.5), 3.74 (s, 3H), 3.38−3.29 (m, 1H), 3.21−3.13 (m, 1H), 2.51 (dd, 1H, *J* = 8.7, 3.4), 1.43 (d, 1H, *J* = 3.4), 0.89 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.4, 147.0, 133.6, 121.8, 120.6, 57.9, 54.6, 51.9, 41.7, 31.1, 27.3; IR (neat) 2960, 1730, 1660, 1440, 1365 cm^{-1}; $[\alpha]^{22}_D$ +68.8 (*c* 2.00, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{13}H_{22}NO_2$ (M + H): 224.1651, found: 224.1674.

***tert*-Butyl (2*R*,3*R*)-2-[3-[(Benzyloxy)methyl]-2-vinylaziridin-1-yl]acetate (32).** Prepared from **16** in 62% yield as detailed for **17**. Flash chromatography (heptane:EtOAc 3:1 → 3:2) gave **32** as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz, peaks assigned from a mixture of invertomers) δ 7.30 (m), 5.67 (m, $1H_{maj}$, $1H_{min}$), 5.42 (d, $1H_{maj}$, *J* = 17.0), 5.33 (m $1H_{maj}$, $1H_{min}$), 5.14 (m, $1H_{min}$), 4.56 (m, $2H_{maj}$, $2H_{min}$), 3.79 (m, $1H_{min}$), 3.65 (dd, $1H_{maj}$, *J* = 10.5, 6.0), 3.50 (dd, $1H_{maj}$, *J* = 10.5, 5.5), 3.47 (m, $1H_{min}$), 3.22 (m, $2H_{maj}$, $2H_{min}$), 2.56 (dd, $1H_{maj}$, *J* = 8.5, 3.0), 2.35 (m, $1H_{min}$), 2.14 (m, $1H_{min}$), 1.95 (m, $1H_{maj}$), 1.47 (s, $9H_{maj}$, $9H_{min}$); ^{13}C NMR ($CDCl_3$, 75 MHz, peaks assigned from a mixture of invertomers) δ 169.8, 169.7, 138.3, 137.6, 131.7, 128.4, 127.8, 127.6, 121.5, 116.6, 81.1, 73.1, 72.9, 71.7, 65.9, 54.7, 54.0, 45.5, 44.4, 42.7, 42.3, 28.1, 28.0; IR (neat, from a mixture of invertomers) 2970, 1735 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{18}H_{26}NO_3$ (M + H): 304.1913, found: 304.1921.

***tert*-Butyl (2(2*R*,3*R*))-2-[3-[(Benzyloxy)methyl]-2-[(*Z*)-1-propenyl]aziridin-1-yl]acetate (33).** Prepared from **16** in 56% yield as detailed for **18**. Flash chromatography (heptane:EtOAc 5:1 → 2:1) gave **33** as an inseparable mixture of isomers (*E*:*Z* 1:10). ^{1}H NMR ($CDCl_3$, 400 MHz, peaks assigned from a mixture of invertomers) δ 7.36−7.28 (m, $5H_{maj}$, $5H_{min}$), 5.90−5.81 (m, $1H_{maj}$, $1H_{min}$), 5.28−5.21 (m, $1H_{maj}$, $1H_{min}$), 4.63−4.54 (m, $2H_{maj}$, $2H_{min}$), 3.73−3.64 (m, $1H_{maj}$, $1H_{min}$), 3.55−3.45 (m, $1H_{maj}$, $1H_{min}$), 3.21 (d, $2H_{maj}$, $2H_{min}$, *J* = 1.8), 2.72 (dd, $1H_{maj}$, *J* = 8.7, 2.7), 2.33 (d, $1H_{min}$, *J* = 7.1), 1.92−1.87 (m, $1H_{maj}$, $1H_{min}$), 1.80 (dd, $3H_{maj}$, *J* = 7.0, 1.7), 1.77−1.72 (m, $3H_{min}$), 1.46 (s, $9H_{maj}$, $9H_{min}$); ^{13}C NMR ($CDCl_3$, 100 MHz, from a mixture of invertomers and only major isomer reported) δ 170.3, 138.7, 133.0, 128.8, 128.2, 128.0, 123.8, 81.4, 73.5, 72.4, 55.3, 47.2, 37.8, 28.5, 13.9; IR (neat, from a mixture of invertomers) 2980, 1745 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{19}H_{28}NO_3$ (M + H): 318.2069, found: 318.2069.

***tert*-Butyl (2(2*R*,3*R*))-2-[3-[(Benzyloxy)methyl]-2-[(*E*)-1-propenyl]aziridin-1-yl]acetate (34).** Prepared from **16** in 5% yield as detailed for **19**. Flash chromatography (heptane:EtOAc 6:1 → 4:1) gave **34** as an inseparable mixture of isomers (*E*:*Z* 1.3:1). ^{1}H NMR ($CDCl_3$, 400 MHz, peaks assigned from a mixture of invertomers) δ 7.36−7.28 (m, $5H_{maj}$, $5H_{min}$), 5.91−5.81 (m, $1H_{maj}$), 5.80−5.73 (m, $1H_{min}$), 5.45−5.38 (m, $1H_{min}$), 5.36−5.29 (m, $1H_{maj}$), 4.61−4.52 (m, $2H_{maj}$, $2H_{min}$), 3.73−3.64 (m, $1H_{maj}$, $1H_{min}$), 3.55−3.45 (m, $1H_{maj}$, $1H_{min}$), 3.21 (m, $2H_{maj}$, $2H_{min}$), 2.53 (dd, $1H_{maj}$, *J* = 8.3, 3.3), 2.10−2.05 (m, $1H_{min}$), 1.92−1.86 (m, $1H_{maj}$), 1.74 (dd, $3H_{maj}$, *J* = 6.5, 1.5), 1.77−1.72 (m, $3H_{min}$), 1.46 (s, $9H_{maj}$, $9H_{min}$); ^{13}C NMR ($CDCl_3$, 100 MHz, from a mixture of invertomers and only major isomer reported) δ 170.4, 138.7, 133.6, 128.8, 128.2, 128.0, 124.7, 81.4, 73.5, 72.4, 55.1, 46.0, 42.6, 28.5, 18.6; IR (neat, from a mixture of invertomers) 2980, 1745 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{19}H_{28}NO_3$ (M + H): 318.2069, found: 318.2067.

(2*R,3*R**)-3-[(Benzyloxy)methyl]-2-[[(*tert*-butyldimethylsilyl)oxy]methyl]aziridine (38).** Prepared from **37** in 87% yield as detailed for aziridine **3**. (2*R**,3*R**)-3-azido-1-(benzyloxy)-4-[(*tert*-butyldimethylsilyl)oxy]-2-butanol and (2*R**,3*R**)-3-azido-4-(benzyloxy)-1-[(*tert*-butyldimethylsilyl)oxy]-2-butanol. Flash chromatography (heptane:EtOAc 6:1 → 3:1) gave a mixture of the corresponding silyl ethers. ^{1}H NMR ($CDCl_3$, 400 MHz, peaks assigned from a mixture of regioisomers) δ 7.39−7.32 (m, $5H_{maj}$, $5H_{min}$), 4.62 (s, $2H_{min}$), 4.61 (s, $2H_{maj}$), 3.98−3.94 (m, $1H_{maj}$), 3.92 (d, $1H_{min}$, *J* = 4.4), 3.89 (d, $1H_{maj}$, *J* = 6.3), 3.86 (d, $1H_{min}$, *J* = 6.3), 3.83−3.79 (m, $1H_{min}$), 3.78 (d, $1H_{maj}$, *J* = 4.4), 3.76 (d, $1H_{min}$, *J* = 6.5), 3.70−3.67 (m, $1H_{min}$), 3.66 (s, $1H_{min}$), 3.65 (s, $1H_{min}$), 3.58 (s, $1H_{maj}$), 3.56 (s, $1H_{maj}$), 3.55−3.52 (m, $1H_{maj}$), 2.65 (br s, $1H_{maj}$), 2.54 (br s, $1H_{min}$), 0.92 (s, $9H_{maj}$), 0.91 (s, $9H_{min}$), 0.11 (s, $6H_{maj}$), 0.09 (s, $6H_{min}$); ^{13}C NMR ($CDCl_3$, 100 MHz, from a mixture of regioisomers) δ 138.1, 128.9, 128.3, 128.3, 128.2, 128.2, 74.0, 74.0, 72.3, 71.5, 71.1, 70.8, 64.7, 64.2, 64.1, 62.3, 26.3, 26.2, 26.1, 18.7, 18.6, −5.0, −5.2; IR (neat, from a mixture of regioisomers) 3450, 2920, 2100 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{17}H_{30}N_3O_3Si$ (M + H): 352.2056, found: 352.2054.

Aziridine 38. Flash chromatography (heptane:EtOAc 4:1 → 1:1) gave aziridine **38** in 59% yield as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32−7.27 (m, 5H), 4.57 (AB-q, 2H, *J* = 20.7, 11.9), 3.80−3.67 (m, 1H), 3.65−3.57 (m, 2H), 3.54−3.43 (m, 1H), 2.40 (q, 1H, *J* = 5.9), 2.33 (q, 1H, *J* = 5.9), 1.68 (br s, 1H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.6, 128.8, 128.8, 128.3, 128.1, 73.6, 70.2, 35.6, 26.4, 26.3, 18.8, −4.8, −4.9; IR (neat) 3300, 2920 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{17}H_{30}NO_2Si$ (M + H): 308.2046, found: 308.2041.

***tert*-Butyl (2(2*R**,3*R**))-2-[3-[(Benzyloxy)methyl]-2-[[(*tert*-butyldimethylsilyl)oxy]methyl]aziridin-1-yl]acetate (39).** Prepared from aziridine **38** in 87% yield as detailed for aziridine **6**. Flash chromatography (heptane:EtOAc 8:1 → 1:1) gave **39** as an oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36−7.27 (m, 5H), 4.57 (AB-q, 2H, *J* = 12.2, 11.8), 3.90 (dd, 1H, *J* = 11.1, 5.5), 3.69 (dd, 1H, *J* = 10.6, 6.1), 3.58−3.53 (m, 2H), 3.10 (AB-q, 2H, *J* = 26.0, 16.2), 1.87 (q, 1H, *J* = 6.3), 1.79 (q, 1H, *J* = 6.7), 1.47 (s, 9H), 0.90 (s, 9H), 0.06 (d, 6H, *J* = 3.0); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.8, 138.7, 128.8, 128.2, 128.0, 81.6, 73.6, 69.4, 62.5, 62.2, 44.9, 43.0, 28.5, 26.3, 18.7, −4.8, −4.9; IR (neat) 2930, 1745 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{23}H_{40}NO_4Si$ (M + H): 422.2727, found: 422.2734.

***tert*-Butyl (2(2*R**,3*R**))-2-[3-[(Benzyloxy)methyl]-2-(hydroxymethyl)aziridin-1-yl]acetate (40).** Prepared from **39** in 98% yield as detailed for **11**. Flash chromatography (heptane:EtOAc 1:1 → 1:4) gave alcohol **40** as an oil. ^{1}H NMR ($CDCl_3$,400 MHz) δ 7.37−7.30 (m, 5H), 4.53 (AB-q, 2H, *J* = 26.6, 11.8), 3.79−3.69 (m, 2H), 3.64 (d, 1H, *J* = 16.9), 3.55−3.46 (m, 2H), 2.61 (d, 1H, *J* = 16.9), 1.98 (q, 1H, *J* = 6.6), 1.88−1.82 (m, 1H), 1.66 (s, 1H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$, 100

MHz) δ 171.0, 138.1, 128.9, 128.9, 128.3, 82.5, 73.8, 69.4, 61.9, 60.9, 45.4, 42.3, 28.5; IR (neat) 3480, 2980, 1730 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{17}H_{26}NO_4$ (M + H): 308.1862, found: 308.1862.

***tert*-Butyl (2(2*S**,3*R**))-2-[3-[(Benzyloxy)methyl]-2-vinylaziridin-1-yl]acetate (41).** Prepared from **40** in 92% yield as detailed for **17**. Flash chromatography (heptane:EtOAc 3:1 → 3:2) gave **41** as an oil. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.30 (m, 5H), 5.66 (ddd, 1H, J = 17.2, 10.3, 6.9), 5.39 (dd, 1H, J = 17.2, 1.8), 5.21 (dd, 1H, J = 10.3, 1.8), 4.56 (d, 1H, J = 11.9), 4.48 (d, 1H, J = 11.9), 3.70 (dd, 1H, J = 10.5, 5.6), 3.44 (dd, 1H, J = 10.5, 6.4), 3.20 (d, 1H, J = 16.0), 3.02 (d, 1H, J = 16.0), 2.15 (t, 1H, J = 6.6), 1.95 (dd, 1H, J = 12.2, 6.4), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.1, 138.2, 133.2, 128.3, 127.8, 127.6, 118.4, 81.3, 73.1, 68.6, 61.9, 45.1, 44.5, 28.1; IR (film) 2985, 1735 $cm^{-1;}$ HRMS (CI+). Exact mass calcd for $C_{18}H_{26}NO_3$ (M + H): 304.1913, found: 304.1918.

***tert*-Butyl (2(2*S**,3*R**))-2-[3-[(Benzyloxy)methyl]-2-[(*Z*)-1-propenyl]aziridin-1-yl]acetate (42).** Prepared from **40** in 87% yield as detailed for **18**. Flash chromatography (heptane:EtOAc 5:1 → 2:1) gave **42** as an inseparable mixture of isomers (*E*:*Z* 1:17). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.35−7.27 (m, 5H), 5.74−5.65 (m, 1H), 5.23 (tq, 1H, J = 18.8, 9.6, 1.4), 4.54 (AB-q, 2H, J = 18.9, 11.8), 3.69 (dd, 1H, J = 10.6, 5.8), 3.46 (dd, 1H, J = 10.6, 6.2), 3.22 (d, 1H, J = 16.0), 3.06 (d, 1H, J = 16.0), 2.32 (t, 1H, J = 7.1), 1.97 (q, 1H, J = 6.2), 1.75 (dd, 3H, J = 6.9, 1.6), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 138.7, 129.0, 128.8, 128.2, 128.0, 126.5, 81.7, 73.5, 69.7, 62.5, 45.0, 40.9, 28.5, 14.0; IR (neat) 2980, 1740 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{19}H_{28}NO_3$ (M + H): 318.2069, found: 318.2071.

***tert*-Butyl (2(2*S**,3*R**))-2-[3-[(Benzyloxy)methyl]-2-[(*E*)-1-propenyl]aziridin-1-yl]acetate (43).** Prepared from **40** in 4% yield as detailed for **19**. Flash chromatography (heptane:EtOAc 12:1 → 6:1) gave **43** as an inseparable mixture of isomers (*E*:*Z* 2.1:1). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.36−7.28 (m, 5H), 5.87−5.78 (m, 1H), 5.27 (ddq, 1H, J = 15.4, 7.2, 1.7), 4.60 (d, 1H, J = 11.9), 4.50 (d, 1H, J = 11.9), 3.71 (dd, 1H, J = 10.5, 5.5), 3.43 (dd, 1H, J = 10.5, 6.7), 3.17 (d, 1H, J = 16.1), 3.03 (d, 1H, J = 16.1), 2.11 (t, 1H, J = 6.9), 1.89 (q, 1H, J = 6.3), 1.71 (dd, 3H, J = 6.5, 1.6), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.7, 138.7, 130.1, 128.8, 128.3, 128.0, 126.7, 81.6, 73.5, 69.1, 62.4, 45.0, 40.9, 28.5, 14.0; IR (neat) 2980, 2860, 1740 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{19}H_{28}NO_3$ (M + H): 318.2069, found: 318.2068.

***tert*-Butyl (2*R*,6*S*)-6-*tert*-Butyl-1,2,3,6-tetrahydropyridine-2-carboxylate (44).** To a solution of diisopropylamine (76.2 μL, 0.543 mmol) in THF (5 mL) at 0 °C was added butyllithium (0.308 mL, 0.493 mmol, 1.6M in hexanes), and the resultant solution was stirred for 30 min at 0 °C. The mixture was cooled to −78 °C, and vinylaziridine **17** (59.1 mg, 0.247 mmol) in THF (5 mL) was added dropwise over 5 min. The resultant red-brown solution was stirred for an additional 5 min and was then quenched by addition of pH 7 buffer (1 mL) and allowed to warm to rt. The phases were separated, and the aqueous phase was extracted with Et_2O (2 × 10 mL). The combined organic phases were dried ($MgSO_4$) and concentrated to give tetrahydropyridine **44** (56.1 mg, 95%) that was pure according to ^1H NMR analysis. Flash chromatography (EtOAc:heptane 1:10 → 1:6) gave **44** (49.6 mg) which had the same spectral data as the crude material. ^1H NMR ($CDCl_3$, 300 Mz) δ 5.79 (m, 1H), 5.69 (m, 1H), 3.42 (dd, 1H, J = 10.7, 4.2), 3.12 (m, 1H), 2.25 (m, 1H), 2.11 (m, 1H), 1.98 (br s, 1H), 1.48 (s, 9H), 0.92 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.8, 128.4, 125.5, 80.9, 64.0, 56.4, 33.9, 29.1, 28.1, 26.1; IR (neat) 2950, 1730 cm^{-1}; $[\alpha]^{20}_D$ +71.3 (*c* 2.14, CH_2Cl_2,); HRMS (CI+); calcd for $C_{14}H_{26}NO_2$ (M + H): 240.1964, found: 240.1964

Rearrangement of Vinylaziridine 24. To a solution of vinylaziridine **24** (23 mg, 0.140 mmol) in THF (5 mL) at −78 °C was added KHMDS (0.215 mL, 0.280 mmol, 1.3 M in THF). Stirring was continued for 5 min, and the reaction was then quenched by addition of pH 7 buffer (1 mL). The mixture was warmed to rt and was then poured into pH 7 buffer (3 mL). The mixture was extracted with Et_2O (2 × 7 mL), and the combined organic phases were dried ($MgSO_4$) and concentrated to give the crude product (23 mg) as a mixture of isomers (**45**: **46** 6.6:1, 80%). Flash chromatography (deactivated silica, heptane:EtOAc 20:1 → 5:1) gave **45** (9.4 mg, 41%) and **46** (2.1 mg, 9%).

(2*R*,6*S*)-6-*tert*-Butyl-2-cyano-1,2,3,6-tetrahydropyridine (45). ^1H NMR ($CDCl_3$, 300 MHz) δ 5.76 (m, 2H), 3.82 (dd, 1H, J = 10.7, 3.9), 3.12 (m, 1H), 2.44 (m, 1H), 2.26 (m, 1H), 1.55 (br s, 1H), 0.92 (s, 9H,); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 128.2, 123.8, 120.6, 63.3, 44.2, 34.1, 29.8, 25.9; IR (neat) 3340, 2960, 2250, 1475 cm^{-1}; $[\alpha]^{22}_D$ +41.9 (*c* 0.327, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{10}H_{17}N_2$ (M + H): 165.1392, found: 165.1381.

(2*S*,6*S*)-6-*tert*-Butyl-2-cyano-1,2,3,6-tetrahydropyridine (46). ^1H NMR ($CDCl_3$, 300 MHz) δ 5.79 (m, 1H), 4.21 (dd, 1H, J = 4.6, 1.2), 3.34 (m, 1H), 2.54 (m, 1H), 2.20 (m, 1H), 1.60 (br s, 1H), 0.90 (s, 9H,); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 127.8, 122.2, 120.3, 59.6, 43.9, 34.0, 28.7, 25.9; IR (neat) 2960, 2240, 1465 cm^{-1}; $[\alpha]^{20}_D$ +10.5 (*c* 0.191, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{10}H_{17}N_2$ (M + H): 165.1392, found: 165.1401.

Rearrangement of Vinylaziridine 26. To a solution of **26** (150 mg, 0.637 mmol) in THF (10 mL) at −78 °C was added *s*-BuLi (0.735 mL, 0.955 mmol, 1.3 M in cyclohexane). The red-brown solution was stirred for 15 min at −78 °C followed by quenching the reaction with pH 7 buffer (2 mL). The mixture was allowed to reach room temperature and was then poured into pH 7 buffer (10 mL) and extracted with Et_2O (2 × 15 mL). Drying ($MgSO_4$) and concentration gave the crude product (142 mg, 95%) as a mixture of **47**, **48**, and **49** (**47**:**48**:**49** 1.2:1.8:1). Flash chromatography (deactivated silica, heptane:EtOAc 1:0 → 10:1) gave **48** (67 mg, 45%), **47** (19 mg, 13%) and **49** (5 mg, 3%).

(2*R*,6*S*)-6-*tert*-Butyl-2-[2-(trimethylsilyl)ethynyl]-1,2,3,6-tetrahydropyridine (47). ^1H NMR ($CDCl_3$, 300 MHz) δ 5.76 (m, 1H), 5.67 (m, 1H), 3.65 (dd, 1H, J = 10.0, 4.3), 3.10 (m, 1H), 2.30−2.11 (m, 2H), 1,65 (br s, 1H), 0.93 (s, 9H), 0.18 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 127.8, 125.6, 107.8, 86.7, 64.3, 46.2, 33.8 32.8, 26.1, 0.03; IR (neat) 2980, 2160, 1540 cm^{-1}; $[\alpha]^{24}_D$ +26.5 (*c* 0.77, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{14}H_{26}NSi$ (M + H): 236.1835, found: 236.1831.

(2*S*,6*S*)-6-*tert*-Butyl-2-[2-(trimethylsilyl)ethynyl]-1,2,3,6-tetrahydropyridine (48). ^1H NMR ($CDCl_3$, 300 MHz) δ 5.73 (br s, 2H), 4.04 (dd, 1H, J = 6.1, 2.1), 3.27 (m, 1H), 2.45 (m, 1H), 2.05 (m, 1H), 1,68 (br s, 1H), 0.93 (s, 9H), 0.15 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 127.3, 123.6, 108.2, 86.2, 58.9, 43.7, 33.7, 30.8, 26.2, 0.2; IR (neat) 2900, 2160, 1460 cm^{-1}; $[\alpha]^{25}_D$ −77.0 (*c* 2.78, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{14}H_{26}NSi$ (M + H): 236.1835, found: 236.1835.

(4*S*,5*S*)-5-*tert*-Butyl-3-[(*E*)-(trimethylsilyl)methylene]-4-vinyl-1-pyrroline (49). ^1H NMR ($CDCl_3$, 500 MHz) δ 7.60 (d, 1H, J = 1.8), 5.99 (d, 1H, J = 2.1), 5.69 (ddd, 1H, J = 17.2, 10.2, 8.0), 5.02−4.96 (m, 2H), 3.76 (t, 1H, J = 2.7), 3.19 (m, 1H), 0.92 (s, 9H), 0.13 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.1, 159.5, 140.8, 129.2, 114.6, 90.3, 45.2, 35.5, 26.4, −0.5; IR(neat) 2960, 1580 cm^{-1}; $[\alpha]^{24}_D$ −8.6 (*c* 0.67, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{14}H_{26}NSi$ (M + H): 236.1835, found: 236.1839.

***tert*-Butyl (2*R*,3*R*,6*S*)-6-*tert*-Butyl-3-methyl-1,2,3,6-tetrahydropyridine-2-carboxylate (50).** Prepared from **18** in 94% yield as detailed for **44**. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.66 (dt, 1H, J = 10.2, 4.2), 5.56 (dt, 1H, J = 10.2, 2.0), 3.03 (m, 1H), 2.96 (d, 1H, J = 9.6), 2.28 (m, 1H), 1.98 (br s, 1H), 1.44 (s, 9H), 1.08 (d, 3H, J = 7.0), 0.96 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.8, 132.7, 127.3, 81.1, 64.0, 62.9, 33.9, 33.4, 28.1, 26.2, 18.7; IR (neat) 2950, 1745, 1455 cm^{-1}; $[\alpha]^{20}_D$ −28.6 (*c* 0.39, $CHCl_3$,); HRMS (CI+). Exact mass calcd for $C_{15}H_{28}NO_2$ (M + H): 254.2120, found: 254.2123.

***tert*-Butyl (2*R*,3*S*,6*S*)-6-*tert*-Butyl-3-methyl-1,2,3,6-tetrahydropyridine-2-carboxylate (51).** Prepared from vinylaziridine **19** (*E*:*Z* 1:1) in 92% yield as detailed for **44**. The crude product was obtained as a mixture of **51** and **50** (**51**:**50** 1:1) and flash chromatography (heptane:EtOAc 10:1 → 6:1) gave **51** in 26% yield. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.78 (ddd, 1H, J = 10.0, 5.4, 2.1), 5.61 (dt, 1H, J = 10.0, 1.1), 3.51 (d, 1H, J = 3.5), 3.10 (m, 1H), 2.43 (m, 1H), 1.62 (br s, 1H), 1.44 (s, 9H), 0.97 (d, 3H, J = 6.7), 0.93 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 178.1, 131.8, 126.4, 87.3, 68.0, 63.8, 33.8, 30.1, 28.1, 26.1, 15.1; IR (neat) 2950, 1750, 1455 cm^{-1}; $[\alpha]^{22}_D$ +51.2 (*c* 0.26,

$CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{15}H_{28}NO_2$ (M + H): 254.2120, found: 254.2119.

***tert*-Butyl (2*R*,6*S*)-6-[(Benzyloxy)methyl]-1,2,3,6-tetrahydropyridine-2-carboxylate (52).** Prepared from vinylaziridine **32** in 98% yield as detailed for **44**. Flash chromatography (heptane:EtOAc 3:1 → 2:3) gave **52** (23 mg, 53%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34 (m, 5H), 5.83 (m, 1H), 5.55 (m, 1H), 4.59 (d, 1H, J = 11.9), 4.51 (d, 1H, J = 11.9), 3.68 (m, 1H), 3.56 (dd, 1H, J = 9.0, 4.0) 3.49 (dd, 1H, J = 10.5, 4.5), 3.43 (dd, 1H, J = 12.0, 8.5), 2.86 (br s, 1H), 2.25 (m, 2H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.1, 138.2, 128.4, 127.8, 127.6, 127.7, 126.2, 81.2, 74.0, 73.4, 55.5, 54.7, 29.1, 28.0; IR (neat) 3340, 2985, 1725 cm^{-1}; $[\alpha]^{22}_D$ +22.9 (*c* 3.89, $CDCl_3$); HRMS (CI+). Exact mass calcd for $C_{18}H_{26}NO_3$ (M + H): 304.1913, found: 304.1909.

***tert*-Butyl (2*R*,3*R*,6*S*)-6-[(Benzyloxy)methyl]-3-methyl-1,2,3,6-tetrahydropyridine-2-carboxylate (53).** Prepared from vinylaziridine **33** in 95% yield as detailed for **44**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36−7.27 (m, 5H), 5.66−5.56 (m, 2H), 4.56 (AB-q, 2H, J = 12.0, 6.5), 3.67−3.58 (m, 1H), 3.58−3.53 (m, 1H), 3.46 (dd, 1H, J = 8.5, 1.9), 3.06 (d, 1H, J = 9.6), 2.49−2.39 (m, 1H), 1.89 (br s, 1H), 1.51 (s, 9H), 1.06 (d, 3H, J = 7.0); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.6, 138.6, 133.6, 128.8, 128.2, 128.1, 126.9, 81.7, 73.9, 73.8, 63.9, 54.6, 33.9, 28.5, 19.1; IR (neat); 2970, 1730 cm^{-1}; $[\alpha]^{22}_D$ +37.8 (*c* 2.00, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{19}H_{28}NO_3$ (M + H): 318.2069, found: 318.2071.

***tert*-Butyl (2*R*,3*S*,6*S*)-6-[(Benzyloxy)methyl]-3-methyl-1,2,3,6-tetrahydropyridine-2-carboxylate (54).** Prepared from vinylaziridine **34** (*E*:*Z* 1.3:1) in 94% yield as a mixture of isomers (**54**:**53** 1.2:1) as detailed for **44**. Flash chromatography (deactivated silica, heptane:EtOAc 1:0 → 15:1) gave pure **54** in 27% yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36−7.28 (m, 6H), 5.85−5.80 (m, 1H), 5.53 (dt, 1H, J = 10.0, 1.4), 4.56 (AB-q, 2H, J = 23.8, 11.9), 3.68−3.62 (m, 1H), 3.60 (d, 1H, J = 4.0), 3.54 (dd, 1H, J = 8.8, 4.3), 3.45 (dd, J = 8.8, 7.4), 2.55−2.48 (m, 1H), 1.50 (s, 9H), 1.40 (br s, 1H), 1.00 (d, 3H, J = 6.8); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.2, 138.7, 133.0, 128.8, 128.1, 128.0, 126.9, 81.5, 74.5, 73.8, 59.7, 55.6, 32.6, 28.5, 15.7 ; IR (neat) 2980, 2940, 1735 cm^{-1}; $[\alpha]^{22}_D$ +39.7 (*c* 0.51, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{19}H_{28}NO_3$ (M + H): 318.2069, found: 318.2064.

***tert*-Butyl (4*S*,5*E*)-3-Aza-4-(*tert*-butyl)-7-(ethoxycarbonyl)-2,5-heptadienecarboxylate (57).** Prepared from vinylaziridine **20** in 96% yield as detailed for the rearrangement of aziridine **17**. Flash chromatography (heptane:EtOAc 6:1) gave **57** as an oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55 (s, 1H), 5.80 (dd, 1H, J = 15.5, 8.2), 5.61 (dt, 1H, J = 15.5, 6.9), 4.18 (q, 2H, J = 7.2), 3.37 (d, 1H, J = 8.2), 3.06 (d, 2H, J = 6.9), 1.53 (s, 9H), 1.25 (t, 3H, J = 7.2), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.6, 161.9, 153.8, 132.3, 124.9, 82.9, 82.2, 60.6, 37.9, 34.9, 28.0, 26.7, 14.2; IR (neat) 2940, 1730, 1640 cm^{-1}; $[\alpha]^{22}_D$ +4.6 (*c* 1.31, $CDCl_3$); HRMS (CI+). Exact mass calcd for $C_{17}H_{30}NO_4$ (M + H): 321.2175, found: 321.2184.

***tert*-Butyl (2*S**,6*S**)-6-[(Benzyloxy)methyl]-1,2,3,6-tetrahydropyridine-2-carboxylate (*rac*-58).** Prepared from **41** in 93% yield as a mixture of isomers (*rac*-**52**:*rac*-**58** 1.8:1). Flash chromatography (heptane:EtOAc 3:1 → 2:3) gave *rac*-**58** in 24% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34 (m, 5H), 5.83 (m, 1H), 5.58 (m, 1H), 4.59 (d, 1H, J = 12.2), 4.53 (d, 1H, J = 12.2), 3.77 (m, 1H), 3.55 (t, 1H, J = 5.9) 3.41 (m, 2H), 2.60 (brs, 1H), 2.34 (m, 2H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.7, 142.7, 138.3, 128.4, 127.6, 125.9, 125.8, 81.0, 73.0, 72.3, 51.8, 51.7, 28.1, 27.8; IR (neat) 3350, 2970, 1725 cm^{-1}; HRMS (CI+). Exact mass calcd for $C_{18}H_{26}NO_3$ (M + H): 304.1913, found: 304.1905.

Rearrangement of Vinylaziridine 30. Vinylaziridine **30** (*E*:*Z* 3.2:1) was rearranged in 95% yield as detailed for **26** to give **59**, **60**, **61a**, and **61b** as a mixture of isomers (**59**:**60**:**61a**:**61b** 4.9:2.4:1.4:1). Flash chromatography (deactivated silica, heptane:EtOAc 1:0 → 10:1) gave **59** (28%), **60** (13%), and pyrrolines **61b** and **61a** as an inseparable mixture of isomers (*E*:*Z* 1:1.4, 8%).

(2*S*,3*S*,6*S*)-6-*tert*-Butyl-3-methyl-2-[(2-trimethylsilyl)-ethynyl]-1,2,3,6-tetrahydropyridine (59). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.61 (s, 2H), 3.58 (d, 1H, J = 2.7), 3.19 (m, 1H), 2.20 (m, 1H), 1.51 (br s, 1H), 1.15 (d, 3H, J = 7.1), 0.85 (s, 9H), 0.11 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 129.8, 126.2, 108.4, 86.2, 59.4, 49.8, 35.5, 33.9, 26.4, 19.8, 0.18; IR(neat) 3360, 2950, 2160 cm^{-1}; $[\alpha]^{22}_D$ −2.4 (*c* 1.21, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{15}H_{28}NSi$ (M + H): 250.1991, found: 250.2000.

(2*R*,3*S*,6*S*)-6-*tert*-Butyl-3-methyl-2-[2-(trimethylsilyl)-ethynyl)-1,2,3,6-tetrahydropyridine (60). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.79 (ddd, 1H, J = 10.4, 5.6, 2.3), 5.57 (dd, 1H, J = 10.4, 1.2), 3.78, (d, 1H, J = 3.7), 3.08 (m, 1H), 2.10 (m, 1H), 1.51 (br s, 1H), 1.15 (dd, 3H, J = 6.9, 2.3), 0.93 (s, 9H), 0.19 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 132.0, 126.4, 107.1, 88.0, 64.6, 50.2, 33.7, 33.6, 26.1, 15.4, 0.06; IR(neat) 2960, 2180 cm^{-1}; $[\alpha]^{22}_D$ +104.3 (*c* 0.418, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{15}H_{28}NSi$ (M + H): 250.1991, found: 250.1983.

(4*S*,5*S*)-5-*tert*-Butyl-3-[(*E*)-(trimethylsilyl)methylene]-4-[(*Z*)-1-propenyl]-1-pyrroline (61a). Prepared from **28** in 98% yield as detailed for the rearrangement of vinylaziridine **26**. Flash chromatography (deactivated silica, heptane:EtOAc 1:0 → 20:1) gave 1-pyrroline **61a** (11 mg, 61%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59 (d, 1H, J = 2.1), 5.91 (d, 1H, J = 2.0), 5.36 (dq, 1H, J = 10.8, 6.5), 5.18 (dt, 1H, J = 10.8, 1.7), 3.70 (t, 1H, J = 2.0), 3.38 (app d, 1H, J = 10.2), 1.67 (dd, 3H, J = 6.5, 1.7), 0.92 (s, 9H), 0.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.2, 161.8, 133.2, 128.7, 122.2, 91.4, 39.9, 35.0, 26.7, 14.1, −0.64; IR (neat) 2970, 1595 cm^{-1}; $[\alpha]^{22}_D$ +62.3 (*c* 0.62, $CHCl_3$); HRMS (CI+). Exact mass calcd for $C_{14}H_{26}NSi$ (M + H): 250.1991, found: 250.1992.

(4*S*, 5*S*)-5-*tert*-Butyl-2-[(*E*)-(trimethylsilyl)methylene]-4-[(*E*)-1-propenyl]-1-pyrroline (61b). ^{1}H NMR ($CDCl_3$, 500 MHz, assigned from a mixture of isomers) δ 7.57 (d, 1H, J = 2.2), 5.94 (d, 1H, J = 2.2), 5.45−5.12 (m, 2H), 3.75 (m, 1H), 3.16 (m, 1H), 1.63 (br s, 3H), 0.92 (s, 9H), 0.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz, assigned from a mixture of isomers) δ 167.1, 160.9, 133.6, 128.7, 125.3, 90.5, 44.2, 35.3, 26.6, 17.8, −0.57; IR (neat) 2950, 1590 cm^{-1}.

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Supporting Information Available: Copies of the ^{13}C NMR spectra of compounds **3**−**20**, **21b**, **22**−**34**, **38**−**54**, and **57**−**61** (55 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; ordering information is given on any current masthead page.

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