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Generation and electrophilic substitution reactions of 3-lithio-2-methyleneaziridines

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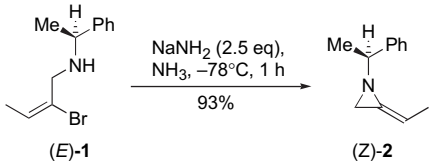
Abstract—2-Methyleneaziridinyl anions can be produced by selective deprotonation of the parent aziridine at C-3 using *sec*-BuLi/TMEDA. Subsequent reaction with a wide variety of electrophiles including MeI, $ICH_2CH_2CH_2CH_2Cl$, $PhCH_2Br$, allyl bromide, Me_3SiCl, Bu_3SnCl, PhCHO and Ph_2CO provides the corresponding C-3 substituted derivatives in moderate to good yields (43–91%). In the case of homochiral methyleneaziridines bearing an (*S*)-α-methylbenzyl group on nitrogen, high levels of diastereocontrol (up to 90%de) can be achieved in this lithiation/alkylation sequence.

1. Introduction

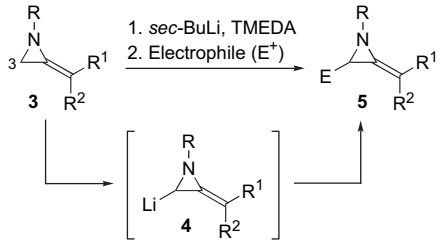
2-Methyleneaziridines are emerging as powerful vehicles for chemical synthesis. Recently, these highly strained heterocycles have been shown to participate in a number of useful transformations including [3+4] cycloadditions,[1] multi-component reactions,[2] radical cascades,[3] and several palladium-catalysed processes.[4–6] Of course, for these reactions to be of broad scope and utility, concise methods for the synthesis of these N-heterocycles are required. Simple 2-methyleneaziridines can easily be made in high yield by reaction of the corresponding 2-bromoallylamines with sodium amide in liquid ammonia.[7] This remarkable cyclisation tolerates considerable structural variation with respect to the substituents on nitrogen and the double bond, and proceeds with net stereochemical inversion at the trigonal carbon atom undergoing substitution.[8] For example, cyclisation of (*E*)-**1** yields (*Z*)-**2** in excellent yield (Scheme 1). Other routes to the parent heterocycles are also known.[9]

To assemble substrates for Lewis acid catalysed intramolecular [3+4] cycloadditions,[1] efficient routes to methyleneaziridines bearing C-3 substituents were required. The synthesis of such derivatives has little literature precedent.[10] Whilst they might conceivably be prepared by ring closure of the appropriately substituted vinyl bromide in an analogous



Scheme 1. Facile synthesis of C-3 unsubstituted methyleneaziridines by ring closure.

manner to that illustrated in Scheme 1, an alternative approach based upon C-3 functionalisation of a preformed 2-methyleneaziridine appeared more flexible and direct (Scheme 2). Early work by Quast and Weise Vélez had established the potential suitability of this approach by showing that 1-*tert*-butyl-2-methyleneaziridine **3** (R=^{t}Bu; R^1, R^2=H) can be deprotonated with *sec*-butyllithium at −78 °C to give organolithium **4** (R=^{t}Bu; R^1, R^2=H) and further alkylated with a limited range of electrophiles



Scheme 2. Strategy for the functionalisation of C-3 substituted methyleneaziridines.

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(MeOD, MeI or Me_3SiCl) to yield **5** (R=^{t}Bu; R^1, R^2=H; E=D, Me_3Si or Me).[10a] In the present article, the scope and limitations of this approach to C-3 substituted methyleneaziridines are examined in detail. Using a range of different methyleneaziridines and electrophiles, it is determined that this method provides a highly practical approach to many C-3 substituted methyleneaziridines.[11] Moreover, using simple chiral, non-racemic methyleneaziridines (R=(*S*)-CHMePh), useful levels of asymmetric induction can be achieved in this process.

2. Results and discussion

2.1. Precursor synthesis

The lithiation/alkylation reactions of wide range of methyleneaziridines have been studied. Eleven different methyleneaziridines **2**, **6–13** were prepared for use in these investigations (Fig. 1). In most instances, the compounds were made according to published procedures by sodium amide induced cyclisation of the corresponding 2-bromoallylamine [(*Z*)-**7**,[8] (*E*)-**7**,[8] **10**,[12] **11**,[13] **12**,[13] (*Z*)-**2**,[8] (*E*)-**2**[8] and **13**[2d]]. The examples incorporating the α-methylbenzyl substituent were produced as the (*S*)-enantiomer.

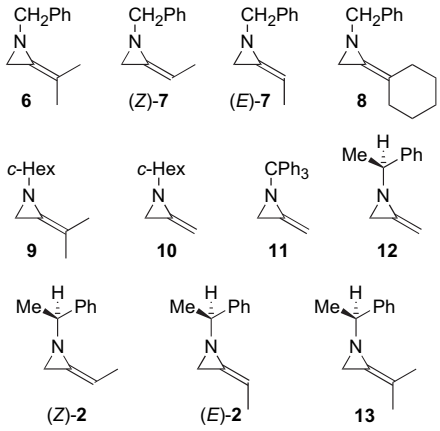
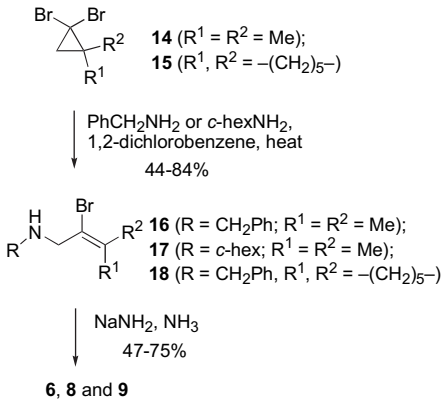


Figure 1. Substrates for lithiation/alkylation studies.

Three new methyleneaziridines, namely **6**, **8** and **9**, were made by a simple two-step sequence. Ring opening[14] of 1,1-dibromocyclopropane **14**[15] with benzylamine and cyclohexylamine yielded vinyl bromides **16** and **17**, respectively (Scheme 3). In a similar manner, opening of **15**[16] with benzylamine provided **18**. For **16** and **18**, the ring opening was performed at 170 °C and high yields (68–84%) were obtained. Using cyclohexylamine (bp 134 °C), the opening was conducted at 120 °C, which may account for the reduced yield of **17** (44%). Ring closure of bromides **16–18** with sodium amide[7,8] proceeded uneventfully to provide methyleneaziridines **6**, **8** and **9** in moderate to good yields.

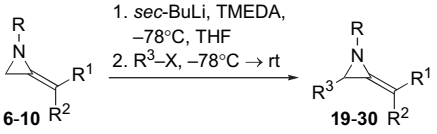
2.2. Lithiation/electrophilic substitution reactions using simple methyleneaziridines

In the original study by Quast and Weise Vélez, it was established that complete lithiation of 1-*tert*-butyl-2-methyleneaziridine at C-3 could be accomplished by treatment



Scheme 3. Synthesis of new methyleneaziridines **6**, **8** and **9**.

with 1.5–2.0 equiv of *sec*-BuLi/tetramethylethylenediamine (TMEDA) in diethyl ether at −78 °C for 7.5 h.[10a] Herein, the lithiation of **6–10** was achieved under very similar conditions and was conducted in THF at −78 °C using a small excess of *sec*-BuLi (1.1–1.5 equiv) and TMEDA (1.1–1.2 equiv) as cosolvent. Complete lithiation at C−3 was achieved in ≤6 h under these conditions. Quenching the lithiated methyleneaziridines with electrophiles and warming to room temperature provided the C-3 substituted products **19–30** in good to excellent yields (Scheme 4 and Table 1). In most cases, a small excess of the electrophile was used (1.2–1.5 equiv). However, for the synthesis of aziridines **29** and **30**, the electrophile was used as the limiting reagent (0.9 equiv). This was necessary because aziridines **28–30** could not be purified by chromatography due to their instability, and excess 1-chloro-4-iodobutane and tributyltin chloride were difficult to remove by distillation. The range of carbon-based electrophiles that can be used in this chemistry is quite broad. Successful alkylations were realised using a variety of alkyl iodides (Table 1, entries 1, 2, 8 and 12), benzyl bromide (Table 1, entry 11), benzophenone (Table 1, entry 4) and benzaldehyde (Table 1, entry 3). In the case of 1-chloro-4-iodobutane, selective displacement of the iodide was observed (Table 1, entry 12). No diastereoselectivity was witnessed in the reaction with benzaldehyde and **21** was produced as ca. 1:1 mixture of diastereomers. Heteroatom-based electrophiles can also be used (Table 1, entries 5 and 13). This chemistry accommodates considerable changes in the methyleneaziridine structure. Variation in the extent of substitution of the exocyclic double bond is well tolerated (Table 1, entries 1, 6–8 and 11). Furthermore, changes in the nature of the N-substituent are possible (Table 1, entry 1 and 9) although no reaction is witnessed with *N*-trityl-2-methyleneaziridine (Table 1, entry 14). The selective lithiation of *N*-benzyl substituted derivatives **6–9** at C-3 is especially notable, with no competitive benzylic deprotonation being observed. Unfortunately, initial attempts to extend this chemistry to the synthesis of 3,3′-disubstituted



Scheme 4. Functionalisation of simple methyleneaziridines via deprotonation/alkylation.

Table 1. Alkylation of simple methyleneaziridines

Entry	Aziridine	R	R^1	R^2	Electrophile	Product	R^3	%Yield[a]
1	**6**	CH_2Ph	Me	Me	MeI	**19**	Me	79
2	**6**	CH_2Ph	Me	Me	(*E*)-PhCH=CH$CH_2CH_2CH_2I$	**20**	$CH_2CH_2CH_2CH$=CHPh	73
3	**6**	CH_2Ph	Me	Me	PhCHO	**21**	CH(OH)Ph	74[b]
4	**6**	CH_2Ph	Me	Me	Ph_2CO	**22**	$C(OH)Ph_2$	73
5	**6**	CH_2Ph	Me	Me	Me_3SiCl	**23**	$SiMe_3$	63
6	(*Z*)-**7**	CH_2Ph	Me	H	Ph_2CO	(*Z*)-**24**	$C(OH)Ph_2$	62
7	(*E*)-**7**	CH_2Ph	H	Me	Ph_2CO	(*E*)-**24**	$C(OH)Ph_2$	73
8	**8**	CH_2Ph	$-(CH_2)_5-$		(2-furanyl)$CH_2CH_2CH_2I$	**25**	$CH_2CH_2CH_2$(2-furanyl)	61
9	**9**	c-Hex	Me	Me	MeI	**26**	Me	64
10	**9**	c-Hex	Me	Me	Me_3SiCl	**27**	$SiMe_3$	64
11	**10**	c-Hex	H	H	$PhCH_2Br$	**28**	CH_2Ph	86
12	**10**	c-Hex	H	H	$ClCH_2CH_2CH_2CH_2I$	**29**	$CH_2CH_2CH_2CH_2Cl$	70[c]
13	**10**	c-Hex	H	H	Bu_3SnCl	**30**	$SnBu_3$	91[c]
14	**11**	CPh_3	H	H	$PhCH_2Br$	n/a	n/a	0

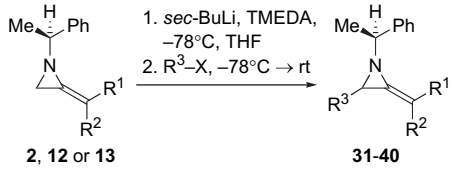
[a] Isolated yield after purification by silica gel chromatography or distillation.
[b] Produced as a separable mixture of two diastereomers (**21a**: 35%; **21b**: 39%).
[c] Yield based upon electrophile which was used as limiting reagent (0.9 equiv).

methyleneaziridines by repeating the lithiation/alkylation sequence on the alkylated products have not been fruitful.

2.3. Diastereocontrolled lithiation/alkylation reactions

Since a new asymmetric centre is produced at C-3 during the lithiation/alkylation sequence (Scheme 2), it was of interest to establish if any stereochemical control could be achieved in this transformation. Indeed, Quast and Weise Vélez had attempted this in the lithiation/alkylation reactions of 1-methyl-2-methyleneaziridine by using an external chiral ligand [(*S*,*S*)-(+)-1,4-bis(dimethylamino)-2,3-dimethoxybutane] as cosolvent. Unfortunately, the levels of enantioselectivity achieved were very modest (12.4% ee).[10b,17] We reasoned that much better levels of asymmetric induction might be achieved by incorporating a chiral, nonracemic element within the nitrogen substituent of the aziridine such that it might exert influence and control on the lithiation/alkylation process. For this study, the α-methylbenzyl group was chosen as the chiral control element because of its simplicity, low cost and widespread use in asymmetric synthesis.[18]

The diastereocontrolled alkylation reactions of four chiral methyleneaziridines, namely (*E*)-**2**, (*Z*)-**2**, **12** and **13** were studied (Scheme 5 and Table 2). Treatment of homochiral (*S*)-**12** with *sec*-BuLi and TMEDA in THF for 7 h, then benzyl bromide, provided **31** in good yield but as an inseparable 53:47 mixture of diastereomers (14% de before purification) (Table 2, entry 1). Using benzophenone as electrophile, an increase in diastereoselectivity was witnessed (Table 2, entry 2 cf. entry 1). Interestingly, a similar trend was seen for (*E*)-**2** (Table 2, entry 4 cf. entry 3) and (*Z*)-**2** (Table 2, entry 6 cf. entry 5). Moreover, the introduction of methyl groups on



Scheme 5. Diastereocontrolled deprotonation/alkylation of homochiral methyleneaziridines.

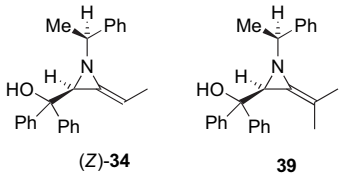
the exocyclic double bond leads to a significant improvement in the level of diastereoselectivity observed (Table 2, entries 1, 3, 5 and 9), with substitution cis to the aziridine nitrogen giving the greatest improvement. Thus, high levels of diastereocontrol (80–90% de) were achieved using 2-isopropylidineaziridine (*S*)-**13** with a range of electrophiles, producing **35**–**40** in moderate to good yields (Table 2, entries 7–12). With the exception of **36**, the alkylated products were readily isolated as single diastereomers after silica gel chromatography. For (*Z*)-**2**, high selectivities (up to 86%) were obtained in some instances (Table 2, entry 6). The relative stereochemistry within (*Z*)-**34** and **39** have been unambiguously established by X-ray crystallography (Fig. 2).[19] All the other alkylated aziridines **31**–**40** are tentatively assigned as having the same configuration at C-3 in the major diastereomer.

The origin of the large differences in the levels of diastereoselectivity observed in the lithiation/alkylation of aziridines (*E*)-**2** and (*Z*)-**2**, **12** and **13** remains unclear. As aziridinyl anions are normally configurationally stable, we suggest that the selectivity in these reactions most likely arises from diastereocontrol in the initial lithiation of the aziridine ring. At first glance, the methyl groups on the alkene terminus appear too remote to exert any increased bias in the stereoselectivity of this process. However, the stereochemical analysis is complicated by the fact that these enantiomerically pure methyleneaziridines exist as mixtures of diastereomers as a result of N-inversion. In an attempt to ascertain if the dynamics of nitrogen inversion play a role in the selectivity of the lithiation process, we have quantified the effect of alkene substitution on the rate of inversion. To simplify the analysis, *N*-benzyl substituted derivatives **6**, (*Z*)-**7**, (*E*)-**7** and *N*-benzylmethyleneaziridine (**41**)[12] were used as the populations of the N-invertomers were equal. The ^1H NMR spectra of the methyleneaziridines were recorded over a range of temperatures at 500 MHz and rate constants obtained for the exchanging signals ascertained by line shape matching with simulated spectra produced using WINDNMR.[20] From the rate constants, the Gibbs free energy of activation ($\Delta G^{\ddagger}$) for the inversion process was determined for each aziridine by use of Eyring plots. The following data were obtained: **41**, $\Delta G^{\ddagger}$=43.5 kJ mol^{-1};

Table 2. Diastereoselective alkylations with homochiral methyleneaziridines

Entry	Aziridine	R^1	R^2	Electrophile	Product	R^3	%Yield[a]	Crude %de[b]
1	**12**	H	H	$PhCH_2Br$	**31**	CH_2Ph	70[c]	14
2	**12**	H	H	Ph_2CO	**32**	$C(OH)Ph_2$	70[d,e]	56
3	(*E*)-**2**	H	Me	$PhCH_2Br$	(*E*)-**33**	CH_2Ph	51[f]	26
4	(*E*)-**2**	H	Me	Ph_2CO	(*E*)-**34**	$C(OH)Ph_2$	68[d]	56
5	(*Z*)-**2**	Me	H	$PhCH_2Br$	(*Z*)-**33**	CH_2Ph	59[f]	48
6	(*Z*)-**2**	Me	H	Ph_2CO	(*Z*)-**34**	$C(OH)Ph_2$	83[d]	86
7	**13**	Me	Me	MeI	**35**	Me	47	80
8	**13**	Me	Me	BuI	**36**	Bu	53[g]	n.d.
9	**13**	Me	Me	$PhCH_2Br$	**37**	CH_2Ph	68	88
10	**13**	Me	Me	$CH_2{=}CHCH_2Br$	**38**	$CH_2CH{=}CH_2$	63	84
11	**13**	Me	Me	Ph_2CO	**39**	$C(OH)Ph_2$	43[d]	88
12	**13**	Me	Me	Me_3SiCl	**40**	$SiMe_3$	80	90

[a] Isolated yield of major diastereomer after purification by silica gel chromatography unless otherwise stated.
[b] Ratio determined by ^1H NMR analysis prior to purification.
[c] Isolated as a 53:47 mixture of diastereomers.
[d] To remove excess Ph_2CO, treated with $NaBH_4$ in EtOH prior to purification.
[e] Isolated as a 80:20 mixture of diastereomers.
[f] Combined yield of separated diastereomers.
[g] Isolated as a 93:7 mixture of diastereomers.



(*Z*)-**34** **39**

Figure 2. Determination of relative stereochemistry in (*Z*)-**34** and **39** by X-ray crystallography.

(*Z*)-**7**, $\Delta G^{\ddagger}$=52.0 kJ mol^{-1}; (*E*)-**7**, $\Delta G^{\ddagger}$=54.2 kJ mol^{-1} and **6**, $\Delta G^{\ddagger}$=57.2 kJ mol^{-1} (at 298 K). From these measurements, it is apparent that the N-inversion barrier is raised by alkene substitution. However, it remains to be established if this is an important factor in the observed changes in diastereoselectivity witnessed in the lithiation/alkylation reactions of (*E*)- and (*Z*)-**2**, **12** and **13** and work focused on uncovering the origin of the selectivity in these reactions is ongoing.

3. Conclusions

It has been established that lithiation/alkylation of methyleneaziridines provides a convenient method for the synthesis of a wide range of C-3 substituted derivatives. Good yields are obtained in many cases and the reaction tolerates considerable variation in the structure of both the methyleneaziridine and the electrophile. Highly diastereoselective alkylations can be achieved with α-methylbenzyl substituted methyleneaziridines (up to 90% de). The best levels of selectivity arise when the alkene substituent cis to the aziridine nitrogen is larger than a hydrogen. This chemistry provides a general approach to C-3 substituted methyleneaziridines and as such will assist in the development of new applications of these N-heterocycles in synthesis.

4. Experimental

4.1. General

Anhydrous solvents were purchased in Sure/Seal™ bottles from Sigma–Aldrich Co., or dried prior to use by distillation. All other solvents and reagents were used as received or purified by standard protocols. All experiments were performed under an inert atmosphere in oven-dried glassware. Column chromatography was carried out using Matrex silica 60. Optical rotations were determined using an Optical Activity Ltd AA1000 Polarimeter. Melting points were measured using Gallenkamp MPD350 apparatus and are reported uncorrected. Infrared spectra were recorded on a Nicolet MAGNA 550 or Perkin–Elmer 'Spectrum One' FT-IR spectrometer with internal calibration. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Bruker ACF-300 or AM-300; or at 400 and 100 MHz, respectively, on a Bruker DRX-400, DPX-400 or AV-400 spectrometer. Low-resolution mass spectra were recorded on a Kratos Profile HV3 or Micromass Quattro II mass spectrometer fitted with an electron ionisation source, or an Esquire 2000 platform with electrospray ionisation. High-resolution mass spectra were obtained using a Finnigan MAT 95XP, Finnigan MAT 900XLT, Micromass 70-VSEQ or VG-7070E instrument. Elemental analyses were carried out on a Perkin–Elmer 2400 CHN or Carlo Erba 1160 elemental analyser.

4.2. General method A: synthesis of amines 16–18

To a stirred solution of dibromocyclopropane **14** or **15** (1.0 M equiv) in 1,2-dichlorobenzene was added the amine (2.2–3.0 M equiv) and potassium carbonate (1.00–1.05 M equiv). The mixture was then heated at 120 or 170 °C for 65–72 h. On cooling to room temperature, sodium hydroxide (2 M aqueous solution) was added. The mixture was extracted with diethyl ether, the combined organic extracts washed with brine then dried over $MgSO_4$. Diethyl ether was removed under reduced pressure and 1,2-dichlorobenzene by distillation (60 °C/15 mmHg). Further purification by column chromatography gave the title amines.

4.2.1. *N*-(2-Bromo-3-methyl-2-butenyl)-1-benzylamine (16). Compound **14** (5.00 g, 21.9 mmol), benzylamine (5.17 g, 48.2 mmol) and potassium carbonate (3.18 g, 23.0 mmol) in 1,2-dichlorobenzene (40 mL) were reacted according to general method A for 72 h at 170 °C. After

work-up, column chromatography (10% EtOAc in petroleum ether) gave **16** (4.68 g, 84%) as a pale yellow oil. IR (film) 3448, 2978, 2932, 1735, 1644 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.40–7.26 (m, 5H), 3.74 (s, 2H), 3.59 (s, 2H), 1.96 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 140.4, 134.1, 128.8, 128.7, 127.4, 121.9, 53.0, 51.9, 25.9, 21.0; MS (CI) *m/z* 254 (MH^+: ^{81}Br), 252 (MH^+: ^{79}Br); HRMS (CI) calcd for $C_{12}H_{17}BrN$ 254.0544, found 254.0537.

4.2.2. *N*-(2-Bromo-3-methyl-2-butenyl)-1-cyclohexylamine (17). Compound **14** (10.0 g, 43.9 mmol), cyclohexylamine (9.58 g, 96.6 mmol) and potassium carbonate (6.08 g, 44.0 mmol) in 1,2-dichlorobenzene (40 mL) were reacted according to general method A for 72 h at 120 °C. After work-up, column chromatography pretreated with triethylamine (10% EtOAc and 0.5% Et_3N in petroleum ether) gave **17** (4.76 g, 44%) as a pale orange oil. IR (film) 3329, 2929, 2852, 1444, 1111, 1009 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 3.54 (s, 2H), 2.36 (m, 1H), 1.88 (s, 3H), 1.81 (s, 3H), 1.81–1.79 (m, 2H), 1.77–1.68 (m, 2H), 1.65–1.50 (m, 2H), 1.25–1.08 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) 132.8, 122.1, 54.5, 50.5, 33.5, 26.1, 25.5, 24.9, 20.5; MS (EI) *m/z* 247 (M^+: ^{81}Br), 245 (M^+: ^{79}Br); HRMS (EI) calcd for $C_{11}H_{20}NBr$ 245.0779, found 245.0770; Anal. Calcd for $C_{11}H_{20}NBr$: C, 53.67; H, 8.19; N, 5.69%. Found: C, 53.41; H, 8.46; N, 5.61%.

4.2.3. *N*-(2-Bromo-2-cyclohexylideneethyl)-1-benzylamine (18). Compound **15** (5.00 g, 18.7 mmol), benzylamine (5.99 g, 55.9 mmol) and potassium carbonate (2.70 g, 19.5 mmol) in 1,2-dichlorobenzene (40 mL) were reacted according to general method A for 65 h at 170 °C. After work-up, column chromatography pretreated with triethylamine (5–10% EtOAc in petroleum ether) gave **18** (3.73 g, 68%) as a pale yellow oil. IR (film) 3336, 3062, 3026, 2923, 2851, 1640, 1604, 1447, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.22–7.36 (m, 5H), 3.70 (s, 2H), 3.60 (s, 2H), 2.45 (br t, J=5.8 Hz, 2H), 2.22 (br t, J=5.9 Hz, 2H), 1.92 (s, 1H), 1.54–1.62 (m, 4H), 1.49–1.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 141.2, 140.1, 128.4, 128.2, 127.0, 119.1, 52.1, 51.4, 35.8, 31.4, 28.0, 27.3, 26.4; MS (EI) *m/z* 293 (M^+: ^{81}Br), 291 (M^+: ^{79}Br); HRMS (EI) calcd for $C_{15}H_{20}BrN$ 293.0779, found 293.0779.

4.2.4. 1-Benzyl-2-(1-methylethylidene)aziridine (6). A three-necked flask was fitted with a cold-finger condenser and a gas inlet. Iron(III) nitrate nonahydrate (12.0 mg, 0.03 mmol) was added and the system was flushed with $CaCl_2$ dried ammonia. A dry ice/acetone mixture was added to the condenser and ammonia (50 mL) was condensed into the flask. Sodium (0.600 g, 26.1 mmol) was added in small portions, each time waiting for the disappearance of the blue colouration prior to the next addition. After cooling to −78 °C, a solution of **16** (2.65 g, 10.4 mmol) in a small volume of diethyl ether was added slowly to the grey suspension. After 1 h, the mixture was diluted with diethyl ether and quenched by the dropwise addition of water (*Caution*). After the ammonia had evaporated, diethyl ether was added and the mixture was stirred for 2 min. The organic phase was separated and washed successively with 0.1 M acetic acid, 10% NaOH and brine, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure to give the crude product, which was purified by bulb-to-bulb distillation to afford **6** (1.31 g, 73%) as a pale yellow oil. IR (film) 1799, 1496, 1452 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6 at 90 °C) 7.36–7.25 (m, 5H), 3.62 (s, 2H), 2.06 (s, 2H), 1.72 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 138.9, 128.4, 128.2, 127.1, 124.2, 104.1, 62.4, 31.7, 20.4, 19.1; MS (CI) *m/z* 173 (M^+); HRMS (CI) calcd for $C_{12}H_{16}N$ (MH^+) 174.1282, found 174.1276; Anal. Calcd for $C_{12}H_{16}N$: C, 83.40; H, 8.80; N, 8.15%. Found: C, 83.20; H, 8.75; N, 8.10%.

4.2.5. *N*-Benzyl-2-cyclohexylideneaziridine (8). A three-necked flask was fitted with a cold-finger condenser and a gas inlet. Iron(III) nitrate nonahydrate (3.4 mg, 8.42 μmol) was added and the system was flushed with $CaCl_2$ dried ammonia. A dry ice/acetone mixture was added to the condenser and ammonia (40 mL) was condensed into the flask. Sodium (0.195 g, 8.48 mmol) was added in small portions, each time waiting for the disappearance of the blue colouration prior to the next addition. A solution of **18** (1.00 g, 3.40 mmol) in Et_2O (2 mL) was added slowly to the grey suspension, which was subsequently stirred for 1.5 h. The mixture was diluted with diethyl ether (20 mL) and quenched by the dropwise addition of water (10 mL) (*Caution*). After the ammonia had evaporated, diethyl ether (20 mL) was added and the mixture was stirred for 2 min. The organic phase was separated and washed successively with 0.1 M acetic acid (20 mL), 10% NaOH (20 mL) and brine (20 mL), dried over $MgSO_4$ and filtered. Removal of the solvent under reduced pressure followed by column chromatography (5–10% EtOAc in petroleum ether) gave **8** (0.340 g, 47%) as a pale yellow oil. IR (film) 3063, 3028, 2921, 2850, 1792, 1599, 1446, 1276 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.42–7.30 (m, 5H), 3.89 (br s, 1H), 3.51 (br s, 1H), 2.74–1.85 (m, 6H), 1.63–1.54 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) 138.9, 128.4, 128.3, 127.2, 121.4, 112.1, 62.8, 31.3, 30.2, 28.0, 27.8, 26.6; MS (EI) *m/z* 213 (M^+); HRMS (EI) calcd for $C_{15}H_{19}N$ 213.1518, found 213.1519.

4.2.6. 2-Isopropylidene-1-(cyclohexyl)aziridine (9). To a three-necked flask fitted with a cold-finger condenser and a gas inlet was added sodium amide (9.93 g, 255 mmol). The system was flushed with $CaCl_2$ dried ammonia then a dry ice/acetone mixture was added to the condenser and ammonia (90 mL) was condensed into the flask. Compound **17** (2.10 g, 8.53 mmol) was added, then the mixture stirred for 3 h. Diethyl ether was added followed by the dropwise addition of water (*Caution*). After the ammonia had evaporated, water and diethyl ether were added and the mixture stirred for 2 min. The organic phase was separated and the aqueous phase extracted with diethyl ether (2×). The combined organic extracts were washed successively with 10% NaOH and brine, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure to give the crude product, which was purified by bulb-to-bulb distillation (90 °C/1 mmHg) to afford **9** (1.05 g, 75%) as a colourless oil. IR (film) 3027, 2929, 2852, 1792, 1444, 1367, 1229, 1127, 1019 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 2.05–1.84 (m, 3H), 1.79 (s, 3H), 1.78–1.71 (m, 3H), 1.72 (s, 3H), 1.70–1.61 (m, 1H), 1.60–1.49 (m, 1H), 1.46–1.28 (m, 2H), 1.25–1.07 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 124.0, 103.0, 66.8, 32.9, 29.1, 25.8,

24.8, 20.9, 19.9; MS (EI) *m/z* 165 (M^+); HRMS (EI) calcd for $C_{11}H_{19}N$ 165.1517, found 165.1522.

4.3. General method B: lithiation/electrophile trapping of methyleneaziridines (2, 6–10, 12 and 13)

To a stirred solution of the aziridine (1.0 M equiv) in THF at −78 °C, was added TMEDA (1.1–1.2 M equiv) and *sec*-BuLi (1.1–1.5 M equiv) dropwise. The reaction was stirred at −78 °C for 3.5–7 h, then quenched with the electrophile (0.9–1.5 equiv) and allowed to warm to room temperature overnight. Water was added, the layers separated, and the aqueous phase extracted with diethyl ether (2×). The combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. Purification by column chromatography or bulb-to-bulb distillation provided the title compounds (**19–40**). For some reactions using benzophenone, an additional reductive step was included in the work-up to facilitate removal of excess electrophile (vide infra).

4.3.1. 1-Benzyl-2-isopropylidene-3-methylaziridine (19). Compound **6** (0.173 g, 1 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.15 mL, 1.5 mmol) and TMEDA (0.140 g, 1.2 mmol) in THF (10 mL) for 6 h in accordance with general method B, then iodomethane (0.170 g, 1.2 mmol) was added. After work-up, purification by column chromatography (5% EtOAc and 0.5% Et_3N in petroleum ether) gave **19** (0.148 g, 79%) as a colourless oil. IR (film) 2965, 2923, 1806, 1495, 1452, 1147, 1021, 730, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.37–7.30 (m, 4H), 7.28–7.22 (m, 1H), 4.11 (d, *J*=13.9 Hz, 1H), 3.28 (d, *J*=13.9 Hz, 1H), 2.04 (br s, 1H), 1.75 (s, 3H), 1.71 (s, 3H), 1.29 (d, *J*=5.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.2, 130.4, 128.2, 127.9, 126.8, 103.8, 61.5, 39.4, 20.4, 18.9, 17.4; MS (ES) *m/z* 188 (MH^+); HRMS (ES) calcd for $C_{13}H_{18}N$ 188.1434, found 188.1432.

4.3.2. (*E*)-1-Benzyl-2-isopropylidene-3-(5-phenylpent-4-enyl)aziridine (20). Compound **6** (0.519 g, 3 mmol) was reacted with *sec*-BuLi (1.2 M in hexanes, 3.75 mL, 4.5 mmol) and TMEDA (0.420 g, 3.6 mmol) in THF (20 mL) for 6 h in accordance with general method B, then [(*E*)-5-iodo-pent-1-enyl]benzene (0.979 g, 3.6 mmol) in THF (7 mL) was added. After work-up, purification by column chromatography (5% EtOAc and 0.5% Et_3N in petroleum ether) gave **20** (0.697 g, 73%) as a slightly yellow oil. IR (film) 3027, 2947, 1792, 1486, 1449, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.32–7.28 (m, 9H), 7.24–7.20 (m, 1H), 6.31 (d, *J*=15.8 Hz, 1H), 6.14 (dt, *J*=15.8, 6.8 Hz, 1H), 4.20 (d, *J*=13.3 Hz, 1H), 3.28 (d, *J*=13.3 Hz, 1H), 2.14 (q, *J*=6.8 Hz, 2H), 2.05 (t, *J*=5.7 Hz, 1H), 1.79 (s, 3H), 1.76 (s, 3H), 1.66–1.55 (m, 2H), 1.49–1.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.1, 137.8, 130.6, 130.2, 129.9, 128.5, 128.4, 128.3, 127.1, 126.8, 125.9, 104.0, 62.0, 44.0, 32.6, 31.8, 27.1, 20.6, 19.0; MS (ES) *m/z* 318 (MH^+); HRMS (EI^+) calcd for $C_{23}H_{27}N$ 317.2138, found 317.2142.

4.3.3. (1-Benzyl-2-isopropylideneaziridin-3-yl)phenylmethanol (21). Compound **6** (0.173 g, 1 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.15 mL, 1.5 mmol) and TMEDA (0.140 g, 1.2 mmol) in THF (10 mL) for 6 h in accordance with general method B, then benzaldehyde (0.127 g, 1.2 mmol) was added. After work-up, purification by column chromatography (5% EtOAc and 0.5% Et_3N in petroleum ether) gave **21a** (after washing with *n*-pentane) (0.098 g, 35%) and **21b** (0.109 g, 39%) as white solids. Compound **21a**: mp 101–102 °C; IR (film) 3157, 2858, 1800, 1490, 1452, 1054, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.33–7.23 (m, 10H), 4.42 (dd, *J*=6.0, 4.5 Hz, 1H) 4.13 (d, *J*=12.9 Hz, 1H), 3.27 (d, *J*=12.9 Hz, 1H), 2.41–2.38 (m, 1H), 2.36 (d, *J*=6.0 Hz, 1H), 1.74 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 141.7, 138.5, 128.7, 128.6, 128.3, 127.59, 127.57, 126.03, 125.98, 106.0, 74.4, 61.6, 50.2, 20.5, 19.2; MS (ES) *m/z* 280 (MH^+); HRMS (ES) calcd for $C_{19}H_{22}NO$ 280.1696, found 280.1695. Compound **21b**: mp 102–103 °C; IR (film) 3131, 2851, 1494, 1447, 1252, 1036, 1024, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.34–7.24 (m, 10H), 4.81 (dd, *J*=3.3, 1.5 Hz, 1H), 4.21 (d, *J*=13.5 Hz, 1H), 3.37 (d, *J*=13.5 Hz, 1H), 3.06 (d, *J*=1.5 Hz, 1H), 2.43 (d, *J*=3.3 Hz, 1H), 1.73 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 141.7, 138.3, 128.5, 128.2, 128.1, 127.6, 127.3, 126.0, 124.4, 106.5, 70.5, 60.7, 48.7, 20.7, 19.2; MS (ES) *m/z* 280 (MH^+); HRMS (ES) calcd for $C_{19}H_{22}NO$ 280.1696, found 280.1695.

4.3.4. (1-Benzyl-2-isopropylideneaziridin-3-yl)diphenylmethanol (22). Compound **6** (0.173 g, 1 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.15 mL, 1.5 mmol) and TMEDA (0.140 g, 1.2 mmol) in THF (10 mL) for 6 h in accordance with general method B, then benzophenone (0.219 g, 1.2 mmol) in THF (1 mL) was added. After work-up, purification by recrystallisation (EtOAc/*n*-pentane) gave **22** (0.258 g, 73%) as a white crystalline solid. Mp 128–129 °C; IR (film) 3373, 3017, 2891, 1793, 1491, 1444, 1319, 1123, 1017, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.41 (d, *J*=7.0 Hz, 2H), 7.31–7.13 (m, 13H), 4.04 (d, *J*=13.0 Hz, 1H), 3.79 (s, 1H), 3.65 (d, *J*=13.0 Hz, 1H), 3.08 (s, 1H), 1.64 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.6, 145.2, 137.6, 128.8, 128.3, 127.93, 127.86, 127.4, 126.9, 126.8, 126.5, 126.2, 123.9, 106.7, 74.5, 60.7, 51.0, 20.1, 19.5; MS (ES) *m/z* 356 (MH^+); HRMS (ES) calcd for $C_{25}H_{26}NO$ 356.2009, found 356.2010.

4.3.5. 1-Benzyl-2-isopropylidene-3-trimethylsilylaziridine (23). Compound **6** (0.173 g, 1 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.15 mL, 1.5 mmol) and TMEDA (0.140 g, 1.2 mmol) in THF (10 mL) for 6 h in accordance with general method B, then chlorotrimethylsilane (0.130 g, 1.2 mmol) was added. After work-up, purification by column chromatography (5% EtOAc and 0.5% Et_3N in petroleum ether) gave **23** (0.155 g, 63%) as a colourless oil. IR (film) 2962, 2914, 1789, 1453, 1247, 836, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.35–7.28 (m, 4H), 7.27–7.22 (m, 1H), 4.39 (d, *J*=13.1 Hz, 1H), 2.90 (d, *J*=13.1 Hz, 1H), 1.78 (s, 3H), 1.73 (s, 3H), 1.24 (s, 1H), −0.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) 139.3, 129.4, 128.4, 128.1, 127.0, 101.2, 64.2, 35.7, 20.3, 18.9, −2.8; MS (ES) *m/z* 246 (MH^+); HRMS (ES) calcd for $C_{15}H_{24}NSi$ 246.1673, found 246.1674.

4.3.6. (*Z*)-(1-Benzyl-2-ethylideneaziridin-3-yl)diphenylmethanol (24). Compound (*Z*)-**7** (0.200 g, 1.26 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.25 mL, 1.63 mmol) and TMEDA (0.174 g, 1.50 mmol) for 5 h in

THF (10 mL) according to general method B, then benzophenone (0.297 g, 1.63 mmol) in THF (1 mL) was added. To remove unreacted benzophenone, the crude material was dissolved in EtOH (20 mL) and cooled to 0 °C. Sodium borohydride (0.108 g, 2.85 mmol) was added and the mixture allowed to warm to room temperature. After stirring for 4 h, the reaction was quenched by the dropwise addition of NH_4Cl solution, then basified using $NaHCO_3$ solution. The resulting mixture was extracted with Et_2O (3×25 mL) and the combined organic phases washed with brine (75 mL), dried ($MgSO_4$) and evaporated. Column chromatography (2% EtOAc in petroleum ether) gave (*Z*)-**24** (0.267 g, 62%) as a colourless oil, which crystallised on standing. Mp 87–89 °C; IR (film) 3444, 3058, 3028, 1785, 1600, 1493, 1447 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.36–7.08 (m, 15H), 5.13 (q, *J*=6.8 Hz, 1H), 4.03 (d, *J*=13.1 Hz, 1H), 3.66 (s, 1H), 3.63 (d, *J*=13.1 Hz, 1H), 2.93 (s, 1H), 1.69 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 146.4, 144.7, 137.0, 129.8, 128.9, 128.3, 128.1, 128.0, 127.5, 127.3, 126.8, 126.3, 97.0, 74.8, 60.3, 50.2, 13.4; MS (ES) *m/z* 342 (MH^+); HRMS (ES) calcd for $C_{24}H_{24}NO$ 342.1852, found 342.1855; Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10%. Found: C, 84.34; H, 6.80; N, 4.00%.

4.3.7. (*E*)-(1-Benzyl-2-ethylideneaziridin-3-yl)diphenylmethanol (24). Compound (*E*)-**7** (0.200 g, 1.26 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.25 mL, 1.63 mmol) and TMEDA (0.174 g, 1.50 mmol) in THF (10 mL) for 5 h according to general method B, then benzophenone (0.297 g, 1.63 mmol) in THF (1 mL) was added. To remove unreacted benzophenone, the crude material was dissolved in EtOH (20 mL) and cooled to 0 °C. Sodium borohydride (0.108 g, 2.85 mmol) was added and the mixture allowed to warm to room temperature. After stirring for 4 h, the reaction was quenched by the dropwise addition of NH_4Cl solution, then basified using $NaHCO_3$ solution. The resulting mixture was extracted with Et_2O (3×25 mL) and the combined organic phases washed with brine (75 mL), dried ($MgSO_4$) and evaporated. The product was purified (2% EtOAc in petroleum ether) to give a colourless oil, which crystallised on standing. Recrystallisation from acetone/water gave (*E*)-**24** (0.316 g, 73%) as clear colourless crystals. Mp 83–86 °C; IR (film) 3446 (br), 3060, 3028, 1782, 1600, 1494, 1449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.37–7.14 (m, 15H), 5.09 (q, *J*=6.8 Hz, 1H), 3.82 (d, *J*=12.9 Hz, 1H), 3.68 (d, *J*=12.9 Hz, 1H), 3.64 (s, 1H), 3.03 (s, 1H), 1.26, (d, *J*=6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 146.9, 145.4, 138.1, 130.3, 129.0, 128.8, 128.5, 128.4, 127.9, 127.5, 127.1, 126.7, 97.7, 75.0, 62.0, 50.9, 14.4; MS (CI) *m/z* 342 (MH^+); HRMS (CI) calcd for $C_{24}H_{24}NO$ 342.1852, found 342.1861.

4.3.8. 1-Benzyl-2-cyclohexylidene-3-[3-(furan-2-yl)propyl]aziridine (25). Compound **8** (0.460 g, 2.16 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 2.5 mL, 3.24 mmol) and TMEDA (0.300 g, 2.58 mmol) in THF (20 mL) for 5 h in accordance with general method B, then 1-iodo-3-(furan-2-yl)propane (560 mg, 2.37 mmol) was added. After work-up, purification by column chromatography (1.5% EtOAc and 0.5% Et_3N in petroleum ether) gave **25** (0.423 g, 61%) as a pale yellow oil. IR (film) 3086, 3062, 3028, 2923, 2850, 1794, 1592, 1446 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.40–7.29 (m, 6H), 6.28 (dd, *J*=3.1, 1.9 Hz, 1H), 5.92 (dd, *J*=3.1, 0.7 Hz, 1H), 4.16 (d, *J*=13.3 Hz, 1H), 3.22 (d, *J*=13.3 Hz, 1H), 2.57 (m, 2H), 2.21 (m, 4H), 2.05 (br s, 1H), 1.66–1.54 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.1, 140.7, 139.1, 128.5, 128.3, 127.1, 127.0, 112.3, 110.0, 104.7, 62.5, 43.4, 31.8, 31.6, 30.1, 28.2, 27.9, 27.6, 26.6, 25.8; MS (EI) *m/z* 322 (MH^+); HRMS (EI) calcd for $C_{22}H_{26}NO$ 320.2014, found 320.2014.

4.3.9. 1-Cyclohexyl-2-isopropylidene-3-methylaziridine (26). Compound **9** (0.200 g, 1.21 mmol) was reacted with *sec*-BuLi (1.0 M in cyclohexane/hexane (98/2), 1.58 mL, 1.58 mmol) and TMEDA (0.169 g, 1.45 mmol) in THF (10 mL) for 5 h in accordance with general method B, then iodomethane (0.258 g, 1.82 mmol) was added. After work-up, purification by column chromatography (0.5% Et_3N in petroleum ether) gave **26** (0.138 g, 64%) as a yellow oil. IR (film) 2924, 2852, 1798, 1444, 1173, 1147, 891 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) 2.30–2.14 (m, 1H), 1.91 (s, 3H), 1.87 (s, 3H), 1.88–1.72 (m, 5H), 1.68–1.46 (m, 3H), 1.36 (d, *J*=5.6 Hz, 3H), 1.30–1.13 (m, 3H); ^{13}C NMR (100 MHz, C_6D_6) 131.6, 100.9, 66.1, 36.3, 33.6, 32.8, 26.1, 24.7 (2C), 21.0, 19.7, 18.3; MS (CI) *m/z* 180 (MH^+); HRMS (CI) calcd for $C_{12}H_{22}N$ 180.1752, found 180.1749.

4.3.10. 1-Cyclohexyl-2-isopropylidene-3-trimethylsilylaziridine (27). Compound **9** (0.200 g, 1.21 mmol) was reacted with *sec*-BuLi (1.0 M in cyclohexane/hexane (98/2), 1.58 mL, 1.58 mmol) and TMEDA (0.169 g, 1.45 mmol) in THF (10 mL) for 5 h in accordance with general method B, then chlorotrimethylsilane (0.199 g, 1.83 mmol) was added. After work-up, purification by column chromatography (0.5% Et_3N in petroleum ether) gave **27** (0.183 g, 64%) as a colourless oil. IR (film) 2929, 2847, 1777, 1444, 1239, 1106, 866, 840 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) 2.23–2.12 (m, 1H), 1.94 (s, 3H), 1.87 (s, 3H), 1.86–1.75 (m, 3H), 1.74–1.66 (m, 2H), 1.61–1.53 (m, 1H), 1.51–1.42 (m, 1H), 1.31–1.15 (m, 3H), 1.14–1.07 (m, 1H), 0.21 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) 130.0, 99.3, 68.5, 33.9, 33.2, 32.5, 26.1, 24.82, 24.81, 21.1, 19.6, −2.7; MS (EI) *m/z* 237 (M^+); HRMS (EI) calcd for $C_{14}H_{27}NSi$ 237.1913, found 237.1922.

4.3.11. 3-Benzyl-1-cyclohexyl-2-methyleneaziridine (28). Compound **10** (0.535 g, 3.90 mmol) was reacted with *sec*-BuLi (1.4 M in hexanes, 3.06 mL, 4.28 mmol) and TMEDA (0.498 g, 4.29 mmol) in THF (5 mL) for 3.5 h in accordance with general method B, then benzyl bromide (0.733 g, 4.29 mmol) was added. After work-up, purification by filtration through a short plug of basic alumina (petroleum ether) followed by bulb-to-bulb distillation of the unreacted starting materials gave **28** (0.764 g, 86%) as a clear, yellow oil. IR (film) 3028, 2828, 1770, 1496, 1451, 1165, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.34–7.27 (m, 5H), 4.74 (s, 1H), 4.68 (s, 1H), 2.93–2.80 (m, 2H), 2.12 (t, *J*=6.3 Hz, 1H), 1.98–1.88 (m, 1H), 1.85–1.62 (m, 3H), 1.60–1.38 (m, 3H), 1.32–1.07 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) 141.9, 139.3, 128.9, 128.4, 126.4, 82.7, 66.9, 42.6, 39.4, 32.9, 32.4, 25.7, 24.57, 24.51; MS (EI) *m/z* 227 (M^+); HRMS (ES) calcd for $C_{16}H_{22}N$ (MH^+) 228.1752, found 228.1756; Anal. Calcd for $C_{16}H_{21}N$: C, 84.52; H, 9.32; N, 6.16%. Found: C, 84.51; H, 9.64; N, 5.93%.

4.3.12. 3-(4-Chlorobutyl)-1-cyclohexyl-2-methyleneaziridine (29). Compound **10** (0.190 g, 1.39 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.16 mL, 1.51 mmol) and TMEDA (0.175 g, 1.51 mmol) in THF (5 mL) for 3.5 h in accordance with general method B, then 1-chloro-4-iodobutane (0.275 g, 1.26 mmol) was added. After work-up, purification by filtration through a short plug of basic alumina (petroleum ether) followed by bulb-to-bulb distillation of the unreacted starting materials gave **29** (0.200 g, 70% based on electrophile) as a clear, light yellow oil. IR (film) 2931, 2855, 1771, 1449, 1265, 1173, 739 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 4.67 (s, 1H), (s, 1H), 3.55 (t, J=6.6 Hz, 2H), 1.87–1.17 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) 142.1, 82.3, 66.8, 44.9, 41.2, 32.9, 32.5, 32.3, 31.6, 25.7, 24.8, 24.59, 24.57; MS (CI) m/z 230 (MH^+: ^{37}Cl), 228 (MH^+: ^{35}Cl); HRMS (ES) calcd for $C_{13}H_{23}NCl$ 228.1519, found 228.1518.

4.3.13. 1-Cyclohexyl-2-methylene-3-(tri-*n*-butylstannyl)-aziridine (30). Compound **10** (0.311 g, 2.27 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.92 mL, 2.50 mmol) and TMEDA (0.290 g, 2.49 mmol) in THF (5 mL) for 3.5 h in accordance with general method B, then tri-*n*-butyltin chloride (0.701 g, 2.16 mmol) was added. After work-up, purification by bulb-to-bulb distillation of the unreacted starting materials followed by filtration through a short plug of basic alumina (petroleum ether) gave **30** (0.833 g, 91% based on electrophile) as a clear light yellow oil. IR (film) 2928, 2854, 1761, 1456, 1362, 1210, 1128, 806 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 4.66 (s, 1H), 4.41 (s, 1H), 1.89–1.19 (m, 24H), 0.95–0.86 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) 143.5, 80.1, 69.8, 33.3, 32.7, 31.7, 29.1, 29.0, 27.3, 25.8, 24.66, 24.62, 13.7, 9.5; MS (CI) m/z 428 (MH^+); HRMS (ES) calcd for $C_{21}H_{42}NSn$ 428.2339, found 428.2342.

4.3.14. (1′*S*,3*R*)- and (1′*S*,3*S*)-3-Benzyl-2-methylene-1-(1-phenylethyl)aziridine (31). Compound (*S*)-**12** (0.200 g, 1.26 mmol) was reacted with *sec*-BuLi (1.0 M in cyclohexane/hexane (98/2), 1.51 mL, 1.51 mmol) and TMEDA (0.175 g, 1.51 mmol) in THF (10 mL) for 7 h in accordance with general method B, then benzyl bromide (0.320 g, 1.87 mmol) was added. After work-up, purification by distillation (170 °C/1 mmHg) gave **31** (0.220 g, 70%) as a 47:53 mixture of diastereomers and as a colourless oil. IR (film) 3062, 3032, 2965, 2919, 2832, 1767, 1495, 1449, 1152, 830, 748, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.37–7.20 (m, 7H), 7.19–7.11 (m, 2H), 7.06–7.01 (m, 1H), 4.87 (s, 0.47H), 4.75 (s, 0.47H), 4.56 (s, 0.53H), 4.26 (s, 0.53H), 3.03 (q, J=6.7 Hz, 0.47H), 2.99 (q, J=6.7 Hz, 0.53H), 2.94–2.86 (m, 1.53H), 2.71 (dd, J=14.3, 6.4 Hz, 0.47H), 2.18 (t, J=6.4 Hz, 0.53H), 2.12 (t, J=6.4 Hz, 0.47H), 1.51 (d, J=6.7 Hz, 1.41H), 1.26 (d, J=6.7 Hz, 1.59H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.94, 143.90, 142.3, 141.6, 139.2, 138.7, 129.0, 128.6, 128.49, 128.47, 128.4, 128.3, 127.2, 127.1, 126.8, 126.4, 126.2, 125.9, 83.5, 83.4, 68.2, 67.6, 43.3, 42.6, 39.1, 38.9, 23.9, 23.1; MS (EI) m/z 249 (M^+); HRMS (CI) calcd for $C_{18}H_{20}N$ 250.1595, found 250.1593.

4.3.15. [(1′*S*,3*R*)- and (1′*S*,3*S*)-2-Methylene-1-(1-phenylethyl)aziridin-3-yl]diphenylmethanol (32). Compound (*S*)-**12** (0.200 g, 1.26 mmol) was reacted with *sec*-BuLi (1.4 M in cyclohexane, 1.08 mL, 1.51 mmol) and TMEDA (0.174 g, 1.50 mmol) in THF (10 mL) for 5 h in accordance with general method B, then benzophenone (0.297 g, 1.63 mmol) in THF (1 mL) was added. After work-up, the residue was redissolved in ethanol (20 mL) and cooled to 0 °C. Sodium borohydride (0.108 g, 2.85 mmol) was added and the solution allowed to warm to room temperature and stirred for 4 h. The reaction was quenched with saturated NH_4Cl solution, then basified using saturated $NaHCO_3$ solution. The resulting mixture was extracted with diethyl ether (3×25 mL) and the combined organic extracts dried ($MgSO_4$), filtered and the solvent removed in vacuo. Impurities were removed by distillation (140 °C/0.2 mmHg) to give **32** (0.301 g, 70%) as a pale yellow oil. IR (film) 3451, 3087, 3060, 3028, 1771, 1658, 1599, 1493, 1448 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.80 (d, J=8.3 Hz, 0.4H), 7.62–6.86 (m, 14.6H), 4.93 (s, 0.2H), 4.73 (s, 0.2H), 4.67 (s, 0.8H), 4.41 (d, J=1.4 Hz, 0.8H), 3.74 (d, J=1.4 Hz, 0.8H), 3.49 (d, J=1.4 Hz, 0.2H), 3.31 (q, J=6.6 Hz, 0.2H), 3.22 (q, J=6.6 Hz, 0.8H), 2.94 (s, 0.8H), 2.90 (s, 0.2H), 1.48 (d, J=6.6 Hz, 0.6H), 0.94 (d, J=6.6 Hz, 2.4H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.4, 145.6, 144.7, 144.4, 143.0, 142.3, 137.3, 136.5, 132.5, 130.1, 128.38, 128.36, 128.2, 128.1, 128.0, 127.7, 127.57, 127.54, 127.48, 127.24, 127.17, 127.1, 127.04, 126.99, 126.7, 126.6, 126.4, 126.2, 84.8, 74.9, 50.4, 49.1, 23.1, 22.7; MS (ES) m/z 342 (MH^+); HRMS (ES) calcd for $C_{24}H_{24}NO$ 342.1852, found 342.1849.

4.3.16. (1′*S*,3*R*)- and (1′*S*,3*S*)-(*E*)-3-Benzyl-2-ethylidene-1-(1-phenylethyl)aziridine (33). Compound (*E*)-**2** (0.218 g, 1.26 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.25 mL, 1.63 mmol) and TMEDA (0.174 g, 1.50 mmol) in THF (10 mL) for 5 h in accordance with general method B, then benzyl bromide (0.279 g, 1.63 mmol) was added. After work-up, purification by column chromatography (10% Et_2O in petroleum ether) gave successively (*E*)-**33a** (0.059 g, 18%) and (*E*)-**33b** (0.108 g, 33%) as colourless oils. Compound (*E*)-**33a**: IR (film) 3062, 3028, 2954, 2921, 2858, 1780, 1686, 1493, 1453 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.40–7.20 (m, 10H), 4.71 (q, J=6.6 Hz, 1H), 2.93–2.85 (m, 3H), 2.20 (t, J=6.3 Hz, 1H), 1.57 (d, J=6.6 Hz, 3H), 1.47 (d, J=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 144.7, 140.0, 135.1, 129.5, 128.8, 128.6, 127.8, 127.4, 126.8, 95.1, 68.4, 44.4, 39.9, 23.6, 14.9; MS (ES) 264 (MH^+); HRMS (EI) calcd for $C_{19}H_{20}N$ 262.1596, found 262.1583. Compound (*E*)-**33b**: IR (film) 3060, 3027, 2968, 2923, 2854, 1776, 1602, 1493 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.40–7.01 (m, 10H), 5.33 (q, J=6.6 Hz, 1H), 2.93 (q, J=6.8 Hz, 1H), 2.93 (dd, J=14.0, 5.9 Hz, 1H), 2.69 (dd, J=14.0, 6.7 Hz, 1H), 2.16 (dd, J=6.7, 5.9 Hz, 1H), 1.65 (d, J=6.7 Hz, 3H), 1.47 (d, J=6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 144.7, 139.4, 135.8, 129.5, 128.7, 128.6, 127.4, 127.1, 126.5, 95.5, 68.9, 43.7, 39.6, 24.4, 15.1; MS (EI) m/z 263 (M^+); HRMS (EI) calcd for $C_{19}H_{21}N$ 262.1596, found 262.1612.

4.3.17. [(1′*S*,3*S*)-(*E*)-2-Ethylidene-1-(1-phenylethyl)aziridin-3-yl]diphenylmethanol (34). Compound (*E*)-**2** (0.218 g, 1.26 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.25 mL, 1.63 mmol) and TMEDA (0.174 g, 1.50 mmol) in THF (10 mL) for 5 h in accordance with general method B, then benzophenone (0.297 g, 1.63 mmol) in

THF (1 mL) was added. After work-up, the residue was redissolved in ethanol (20 mL) and cooled to 0 °C. Sodium borohydride (0.108 g, 2.85 mmol) was added and the solution allowed to warm to room temperature and stirred for 4 h. The reaction was quenched with saturated NH_4Cl solution, then basified using saturated $NaHCO_3$ solution. The resulting mixture was extracted with diethyl ether (3× 25 mL) and the combined organic extracts dried ($MgSO_4$), filtered and the solvent removed in vacuo. Purification by column chromatography (10% Et_2O in petroleum ether) gave (*E*)-**34** (0.302 g, 68%) as a colourless oil. IR (film) 3441 (br), 3057, 2966, 1778, 1598, 1491, 1447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.39–6.92 (m, 15H), 4.78 (q, *J*=6.8 Hz, 1H), 3.97 (s, 1H), 3.16 (q, *J*=6.6 Hz, 1H), 3.09 (s, 1H), 1.37, (d, *J*=6.8 Hz, 3H), 0.98 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 147.0, 145.4, 144.0, 129.9, 128.7, 128.5, 128.4, 127.64, 127.57, 127.4, 126.9, 126.7, 97.4, 74.7, 67.1, 51.2, 23.5, 14.3; MS (EI) *m/z* 355 (M^+); HRMS (EI) calcd for $C_{25}H_{25}NO$ 355.1936, found 355.1952.

4.3.18. (1′*S*,3*R*)- and (1′*S*,3*S*)-(*Z*)-3-Benzyl-2-ethylidene-1-(1-phenylethyl)aziridine (33). Compound (*Z*)-**2** (0.218 g, 1.26 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.25 mL, 1.63 mmol) and TMEDA (0.174 g, 1.50 mmol) in THF (10 mL) for 5 h in accordance with general method B, then benzyl bromide (0.280 g, 1.64 mmol) was added. After work-up, purification by column chromatography (10% Et_2O in petroleum ether) gave successively (*Z*)-**33a** (0.138 g, 42%) and (*Z*)-**33b** (0.057 g, 17%) as colourless oils. Compound (*Z*)-**33a**: IR (film) 3060, 3027, 2968, 2920, 1779, 1601, 1493, 1448, 1306, 1132, 1028, 745, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.40–7.18 (m, 10H), 5.02 (q, *J*=6.8 Hz, 1H), 2.95 (q, *J*=6.6 Hz, 1H), 2.86 (d, *J*=6.4 Hz, 2H), 2.17 (t, *J*=6.4 Hz, 1H), 1.26 (d, *J*=6.6 Hz, 3H), 1.06 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 145.1, 139.4, 135.1, 129.3, 128.78, 128.76, 127.8, 127.6, 126.7, 95.6, 68.4, 44.0, 39.9, 23.7, 13.6; MS (EI) *m/z* 263 (M^+); HRMS (EI) calcd for $C_{19}H_{20}N$ 262.1596, found 262.1590. Compound (*Z*)-**33b**: IR (film) 3063, 3028, 2973, 2928, 1779, 1604, 1494, 1453 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.40–7.00 (m, 10H), 5.18 (q, *J*=6.8 Hz, 1H), 3.18 (q, *J*=6.6 Hz, 1H), 2.84 (dd, *J*=14.0, 5.3 Hz, 1H), 2.62 (dd, *J*=14.0, 7.3 Hz, 1H), 2.17 (dd, *J*=7.3, 5.3 Hz, 1H), 1.90 (d, *J*=6.6 Hz, 3H), 1.57 (d, *J*=6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 144.4, 139.5, 135.8, 129.0, 128.7, 128.6, 127.5, 127.3, 126.5, 95.6, 67.7, 42.4, 39.6, 24.4, 14.4; MS (EI) *m/z* 263 (M^+); HRMS (EI) calcd for $C_{19}H_{20}N$ 262.1596, found 262.1603.

4.3.19. (1′*S*,3*S*)-(*Z*)-2-Ethylidene-1-(1-phenylethyl)aziridin-3-yl)diphenylmethanol (34). Compound (*Z*)-**2** (0.218 g, 1.26 mmol) was reacted with *sec*-BuLi (1.3 M in hexanes, 1.25 mL, 1.63 mmol) and TMEDA (0.174 g, 1.50 mmol) in THF (10 mL) for 5 h in accordance with general method B, then benzophenone (0.297 g, 1.63 mmol) in THF (1 mL) was added. After work-up, the residue was redissolved in ethanol (20 mL) and cooled to 0 °C. Sodium borohydride (0.108 g, 2.85 mmol) was added and the solution allowed to warm to room temperature and stirred for 4 h. The reaction was quenched with saturated NH_4Cl solution, then basified using saturated $NaHCO_3$ solution. The resulting mixture was extracted with diethyl ether (3×25 mL) and the combined organic extracts dried ($MgSO_4$), filtered and the solvent removed in vacuo. Column chromatography (10% Et_2O in petroleum ether) gave (*Z*)-**34** (0.371 g, 83%) as a colourless oil, which crystallised on standing. $[\alpha]_D^{21}$ −11.4 (*c* 2.2, $CHCl_3$); mp 102–105 °C; IR (film) 3422, 3053, 3028, 1782, 1595, 1490, 1445 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) 7.55–7.20 (m, 15H), 5.09 (q, *J*=6.6 Hz, 1H), 3.88 (s, 1H), 3.16 (q, *J*=6.8 Hz, 1H), 2.93 (s, 1H), 1.08 (d, *J*=6.8 Hz, 3H), 0.85 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 146.7, 144.5, 143.8, 129.4, 128.2, 128.0, 127.8 (2C), 127.23, 127.18, 127.0, 126.9, 126.7, 126.0, 97.2, 74.6, 66.3, 50.0, 22.9, 12.9; MS (EI) *m/z* 355 (M^+); HRMS (EI) calcd for $C_{25}H_{25}NO$ 355.1936, found 355.1918; Anal. Calcd for $C_{25}H_{25}NO$: C, 84.45; H, 7.09; N, 3.94%. Found: C, 84.40; H, 7.07; N, 3.92%.

4.3.20. (1′*S*,3*R*)-2-Isopropylidene-3-methyl-1-(1-phenylethyl)aziridine (35). Compound **13** (0.200 g, 1.07 mmol) was reacted with *sec*-BuLi (1.0 M in cyclohexane/hexane (98/2), 1.39 mL, 1.39 mmol) and TMEDA (0.149 g, 1.28 mmol) in THF (8 mL) for 5 h in accordance with general method B, then iodomethane (0.227 g, 1.60 mmol) was added. After work-up, purification by column chromatography (0.5% Et_3N in petroleum ether) gave **35** as a single diastereomer (0.100 g, 47%) and as a yellow oil. $[\alpha]_D^{21}$ −235 (*c* 1.01, $CHCl_3$); IR (film) 3032, 2970, 2919, 2847, 1798, 1449, 1147, 702 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) 7.57–7.53 (m, 2H), 7.31–7.24 (m, 2H), 7.21–7.15 (m, 1H), 2.93 (q, *J*=6.5 Hz, 1H), 1.90 (q, *J*=5.6 Hz, 1H), 1.77 (s, 3H), 1.46 (d, *J*=6.5 Hz, 3H), 1.42 (d, *J*=5.6 Hz, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) 146.0, 131.2, 128.3, 127.5, 127.1, 102.3, 68.2, 37.6, 24.0, 20.8, 19.0, 18.1; MS (CI) *m/z* 202 (MH^+); HRMS (CI) calcd for $C_{14}H_{20}N$ 202.1595, found 202.1605.

4.3.21. (1′*S*,3*R*)- and (1′*S*,3*S*)-3-Butyl-2-isopropylidene-1-(1-phenylethyl)aziridine (36). Compound **13** (0.200 g, 1.07 mmol) was reacted with *sec*-BuLi (1.0 M in cyclohexane/hexane (98/2), 1.39 mL, 1.39 mmol) and TMEDA (0.149 g, 1.28 mmol) in THF (8 mL) for 5 h in accordance with general method B, then 1-iodobutane (0.294 g, 1.60 mmol) was added. After work-up, purification by column chromatography (0.5% Et_3N in petroleum ether) gave **36** as a 93:7 mixture of diastereomers (0.137 g, 53%) and as a yellow oil. IR (film) 3027, 2965, 2929, 2852, 1792, 1449, 1229, 758, 691 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) *Major diastereomer*: 7.59–7.55 (m, 2H), 7.31–7.24 (m, 2H), 7.20–7.13 (m, 1H), 2.93 (q, *J*=6.6 Hz, 1H), 1.94–1.90 (m, 1H), 1.81 (s, 3H), 1.79–1.50 (m, 4H), 1.49 (d, *J*=6.6 Hz, 3H), 1.45–1.36 (m, 2H), 1.32 (s, 3H), 0.99 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) *Major diastereomer*: 146.1, 130.7, 128.3, 127.1 (2C), 102.3, 68.2, 42.6, 32.6, 30.0, 24.2, 22.9, 21.1, 19.1, 14.0; MS (CI) *m/z* 244 (MH^+); HRMS (CI) calcd for $C_{17}H_{26}N$ 244.2065, found 244.2074.

4.3.22. (1′*S*,3*R*)-3-Benzyl-2-isopropylidene-1-(1-phenylethyl)aziridine (37). Compound **13** (0.200 g, 1.07 mmol) was reacted with *sec*-BuLi (1.0 M in cyclohexane/hexane (98/2), 1.39 mL, 1.39 mmol) and TMEDA (0.149 g, 1.28 mmol) in THF (8 mL) for 5 h in accordance with general method B, then benzyl bromide (0.274 g, 1.60 mmol) was added. After work-up, purification by column chromatography (0.5% Et_3N in petroleum ether) gave **37** (0.201 g,

68%) as a single diastereomer and as a colourless oil. $[\alpha]_D^{22}$ −152 (*c* 1.0, $CHCl_3$); IR (film) 3062, 3027, 2960, 2919, 2847, 1787, 1598, 1495, 1444, 1127, 758, 697 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) 7.53–7.51 (m, 2H), 7.39–7.33 (m, 2H), 7.30–7.22 (m, 4H), 7.21–7.15 (m, 2H), 2.97 (dd, *J*=13.8, 5.6 Hz, 1H), 2.92 (dd, *J*=13.8, 6.9 Hz, 1H), 2.86 (q, *J*=6.6 Hz, 1H), 2.15 (dd, *J*=6.9, 5.6 Hz, 1H), 1.72 (s, 3H), 1.30 (s, 3H), 1.25 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) 145.9, 140.0, 130.2, 129.3, 128.36, 128.32, 127.5, 127.1, 126.3, 103.0, 68.2, 44.1, 39.8, 24.1, 21.1, 19.1; MS (EI) *m/z* 277 (M^+); HRMS (EI) calcd for $C_{20}H_{23}N$ 277.1830, found 277.1843.

4.3.23. (1′*S*,3*R*)-3-Allyl-2-isopropylidene-1-(1-phenylethyl)aziridine (38). Compound **13** (0.200 g, 1.07 mmol) was reacted with *sec*-BuLi (1.0 M in cyclohexane/hexane (98/2), 1.39 mL, 1.39 mmol) and TMEDA (0.149 g, 1.28 mmol) in THF (8 mL) for 5 h in accordance with general method B, then allyl bromide (0.189 g, 1.56 mmol) was added. After work-up, purification by column chromatography (0.5% Et_3N in petroleum ether) gave **38** (0.153 g, 63%) as a single diastereomer and as a colourless oil. $[\alpha]_D^{22}$ −210 (*c* 1.03, $CHCl_3$); IR (film) 3073, 3027, 2970, 2919, 2852, 1798, 1644, 1490, 1454, 1372, 1219, 1137, 988, 912, 758, 702 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) 7.55–7.52 (m, 2H), 7.30–7.25 (m, 2H), 7.21–7.16 (m, 1H), 6.10–6.00 (m, 1H), 5.24–5.12 (m, 2H), 2.90 (q, *J*=6.6 Hz, 1H), 2.46 (dd, *J*=6.8, 5.9 Hz, 2H), 1.94 (br t, *J*=5.9 Hz, 1H), 1.78 (s, 3H), 1.46 (d, *J*=6.6 Hz, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) 145.9, 136.0, 129.9, 128.3, 127.5, 127.1, 116.1, 102.9, 68.0, 42.0, 37.6, 24.2, 21.1, 19.1; MS (CI) *m/z* 228 (MH^+); HRMS (CI) calcd for $C_{16}H_{22}N$ 228.1752, found 228.1756.

4.3.24. [(1′*S*,3*S*)-2-Isopropylidene-1-(1-phenylethyl)aziridin-3-yl]diphenylmethanol (39). Compound **13** (0.200 g, 1.07 mmol) was reacted with *sec*-BuLi (1.0 M in cyclohexane/hexane (98/2), 1.39 mL, 1.39 mmol) and TMEDA (0.149 g, 1.28 mmol) in THF (8 mL) for 5 h in accordance with general method B, then benzophenone (0.292 g, 1.60 mmol) in THF (1 mL) was added. After work-up, the residue was redissolved in ethanol (15 mL) and cooled to 0 °C. Sodium borohydride (0.090 g, 2.38 mmol) in ethanol (3 mL) was added and the solution allowed to warm to room temperature and stirred for a further 4 h. The reaction was quenched with NH_4Cl solution. The aqueous phase was basified using $NaHCO_3$ then extracted with diethyl ether. The combined organic phases were dried ($MgSO_4$), and the solvent was removed under reduced pressure. Purification by column chromatography (0.5% Et_3N in petroleum ether) gave **39** as a single diastereomer (0.168 g, 43%) and as a white solid. $[\alpha]_D^{22}$ −111 (*c* 1.01, $CHCl_3$); IR (KBr) 3293, 2975, 2916, 2853, 1444, 1135, 754, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.67–7.56 (m, 4H), 7.40–7.26 (m, 7H), 7.25–7.21 (m, 4H), 4.08 (s, 1H), 3.18 (t, *J*=6.6 Hz, 1H), 3.15 (s, 1H), 1.36 (s, 3H), 1.08 (s, 3H), 0.91 (d, *J*=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 147.0, 145.3, 144.5, 128.3, 128.1, 128.0, 127.3, 127.0, 126.8, 126.3, 126.1, 123.9, 107.0, 74.2, 66.6, 50.7, 23.4, 20.6, 19.5; MS (CI) *m/z* 370 (MH^+); HRMS (CI) calcd for $C_{26}H_{28}NO$ 370.2171, found 370.2185; Anal. Calcd for $C_{26}H_{27}NO$: C, 84.51; H, 7.37; N, 3.79%. Found: C, 84.63; H, 7.55; N, 3.46%.

4.3.25. (1′*S*,3*R*)-2-Isopropylidene-1-(1-phenylethyl)-3-trimethylsilylaziridine (40). Compound **13** (0.200 g, 1.07 mmol) was reacted with *sec*-BuLi (1.0 M in cyclohexane/hexane (98/2), 1.39 mL, 1.39 mmol) and TMEDA (0.149 g, 1.28 mmol) in THF (8 mL) for 5 h in accordance with general method B, then chlorotrimethylsilane (0.175 g, 1.61 mmol) was added. After work-up, purification by column chromatography (0.5% Et_3N in petroleum ether) gave **40** as a single diastereomer (0.222 g, 80%) and as a colourless oil. $[\alpha]_D^{21}$ −133 (*c* 1.07, $CHCl_3$); IR (film) 3062, 3021, 2960, 2919, 2847, 1782, 1490, 1444, 1265, 1091, 1004, 866, 830, 753, 691 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) 7.55–7.52 (m, 2H), 7.30–7.23 (m, 2H), 7.21–7.18 (m, 1H), 2.82 (q, *J*=6.5 Hz, 1H), 1.77 (s, 3H), 1.43 (d, *J*=6.5 Hz, 3H), 1.32 (s, 3H), 1.20 (s, 1H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) 146.0, 129.5, 128.3, 127.5, 127.1, 100.4, 70.3, 33.8, 24.4, 20.8, 18.9, −2.7; MS (CI) *m/z* 260 (MH^+); HRMS (CI) calcd for $C_{16}H_{26}NSi$ 260.1835, found 260.1824.

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