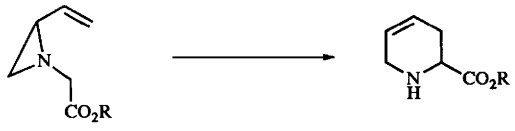
# Synthesis of 4-phenylpiperidines by tandem Wittig olefination–aza-Wittig rearrangement of 2-benzoylaziridines

**Iain Coldham,*[a] Alan J. Collis,[b] Roger J. Mould[a] and Richard E. Rathmell[a]**
[a] *Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, UK*
[b] *Department of Discovery Chemistry, Pfizer Central Research, Sandwich, Kent CT13 9NJ, UK*

A number of routes to 2-vinylaziridines are reported. N-Alkylation of a range of 2-benzoyl-3-alkylaziridines with *tert*-butyl bromoacetate followed by Wittig olefination gave directly a range of 4-phenylpiperidines. The intermediate 2-vinylaziridines rearrange by a [2,3]-aza-Wittig rearrangement to give the 4-phenylpiperidines.

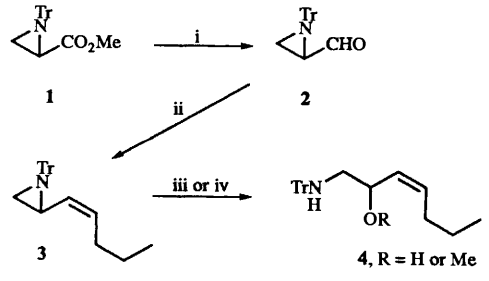
In 1972, Durst *et al.*[1] reported the ring expansion of a β-lactam to a seven-membered ring lactam using the [2,3]sigmatropic rearrangement. Ring expansions of five- and six-membered quaternary ammonium salts by a [2,3]sigmatropic shift are also known.[2] We[3] and others,[4] have been interested in promoting the aza-Wittig rearrangement using tertiary amines. We considered the possibility of effecting the [2,3]sigmatropic shift using vinylaziridines[5] as this would place the breaking C–N bond into a strained three-membered ring (so aiding rearrangement) and give access to the more widespread six-membered cyclic amine products (Scheme 1). In this paper, we



**Scheme 1**

report a one-pot method for this ring expansion of aziridines to piperidines by tandem olefination–aza-Wittig rearrangement of 2-benzoylaziridines to 4-phenylpiperidines. Related work by Åhman and Somfai[6] using lithium diisopropylamide (LDA)-promoted rearrangement of vinylaziridines, prepared from aziridine-2-carbaldehydes has been shown to give excellent yields of the piperidine products.

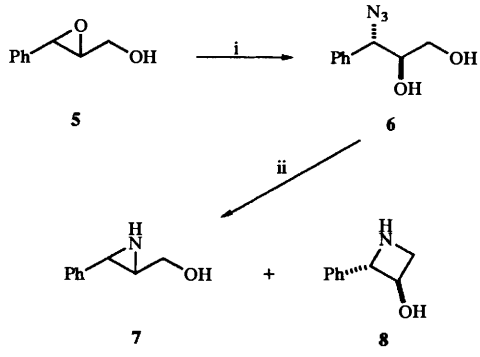
We have investigated a number of routes to N-unsubstituted vinylaziridines which would then be functionalised in preparation for the aza-Wittig rearrangement. At first we looked at the use of serine as a precursor to aziridines. Following known chemistry,[7] we prepared the *N*-trityl aziridine **1**, which was reduced to the aldehyde **2** and converted into the vinylaziridine **3** (4:1 *cis*:*trans*) using the Wittig olefination procedure (Scheme 2). All attempts, however, to cleave the *N*-



**Scheme 2** *Reagents and conditions:* i, DIBAL PhMe, −95 °C, 93%; ii, $BuPPh_3Br$, BuLi, THF, 100%; iii, $CF_3CO_2H$, $CHCl_3$, 85%; iv, $CF_3CO_2H$, $CHCl_3$, MeOH, 68%

trityl group in the presence of the alkene (or aldehyde) were unsuccessful and resulted in ring-opening of the aziridine to the amine **4**. Removal of the trityl group has been reported[7] from the aziridine **1**, although we found that the resulting N-unsubstituted aziridine was volatile and did not undergo alkylation under standard conditions.[8]

We turned our attention to the preparation of vinylaziridines from epoxides using ring-opening by azide and ring-closure by triphenylphosphine.[9] Azide-opening of 3-phenylglycidol **5** gave the regioisomerically-pure azido alcohol **6**, as expected (Scheme 3).[10] Ring-closure with triphenylphosphine gave the aziridine **7**



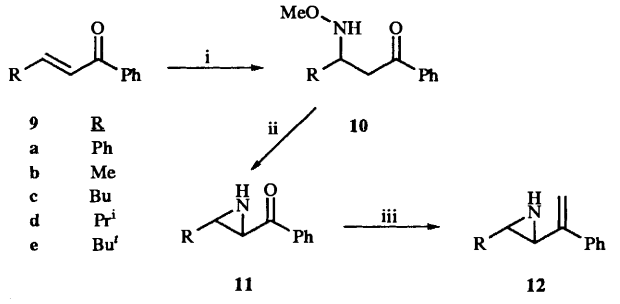
**Scheme 3** *Reagents and conditions:* i, $NaN_3$, MeOH, $H_2O$, $NH_4Cl$, 80%; ii, $Ph_3P$, MeCN, reflux, 6 h, **7** 50% and **8** 10%

together with the azetidine **8**. The isolation of the four-membered ring **8** is interesting and suggests that this could be a useful entry to azetidines in the absence of, or protection of the secondary alcohol. The formation of the azetidine **8** led us to consider the protection of the primary alcohol **5** or **6** as a route to vinylaziridines. This approach has been shown to be successful[6,11] and will be reported in due course. Attempts to prepare vinylaziridines by ring-opening of vinyl epoxides was complicated by competing $S_N2'$ opening of the vinyl epoxides (or rearrangement of the resulting allylic azides by a [3,3]sigmatropic shift), except when this would move the double bond out of conjugation.[12]

An alternative approach to the desired vinylaziridines followed chemistry reported by Nagel *et al.*[13] and Attia *et al.*[14] Addition of methoxylamine to a range of unsaturated phenylketones **9a–e** gave the adducts **10a–e** which were closed to the aziridines **11a–e** using sodium methoxide (Scheme 4, Table 1). In all cases except **10b**, R = Me, closure gave the aziridine *trans*-**11** with no observed aziridine *cis*-**11**. For R = Me, the aziridine **11b** was formed as a 1:1 mixture of stereoisomers (in accord with the literature[14]). Wittig olefination of the keto aziridines **11a–d** gave the vinylaziridines **12a–d** with improved yields over the two cases (R = Ph, Me) reported by Attia *et al.* We were now in a position to investigate

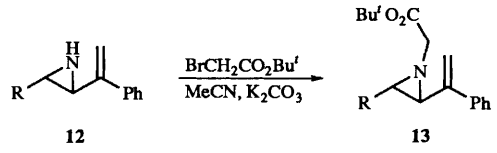
**Table 1** Yields (%) of ketones **10** and aziridines **11** and **12**

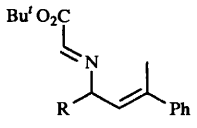
| Entry | R | 10 | 11 | 12 |
|---|---|---|---|---|
| **a** | Ph | 67 | 65 | 83 |
| **b** | Me | 82 | 76 | 93 |
| **c** | Bu | 71 | 49 | 81 |
| **d** | $Pr^i$ | 84 | 82 | 67 |
| **e** | $Bu^t$ | 13 | 36 | — |




**Scheme 4** *Reagents and conditions:* i, $MeONH_2$, $Et_3N$, MeOH; ii, NaOMe, MeOH; iii, $MePPh_3Br$, NaH, DMSO

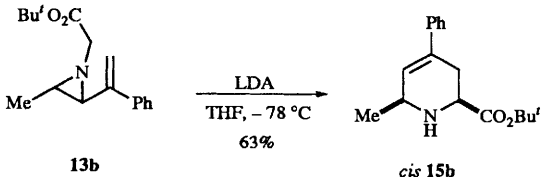
the alkylation and aza-Wittig rearrangement of the vinylaziridines. Alkylation of the vinylaziridines **12a,b** gave the required substrates **13a** (50%, 78% based on recovered **12a**) and **13b** (48%) (Scheme 5). Attempted alkylation of the vinylaziridines




**Scheme 5**

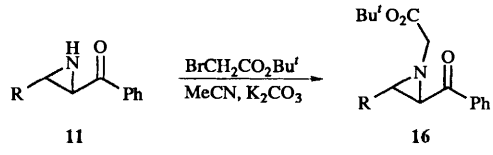
**12c,d** (R = Bu, $Pr^i$) did give the desired N-alkylated products, however, these were unstable and rearranged by a [1,5]-hydrogen shift[15,16] to the imines **14c,d** ($^1H$ NMR $\delta$ 7.69 ppm for imine proton, R = Bu or $Pr^i$). This rearrangement has precedent from related vinylaziridines,[16] although the substrates **13** appear to rearrange at a faster rate than those without the phenyl group at C-2 of the alkene. The vinylaziridine **13b**, R = Me rearranges only slowly at room temperature (< 5% [1,5]-hydrogen shift after 15 min) and was treated with LDA to effect the [2,3]-aza-Wittig rearrangement. We were pleased to find that the aza-Wittig rearrangement–ring expansion of the aziridine to the piperidine was successful and the piperidine *cis*-**15b**, R = Me was isolated as a single stereoisomer (Scheme 6).




**Scheme 6**

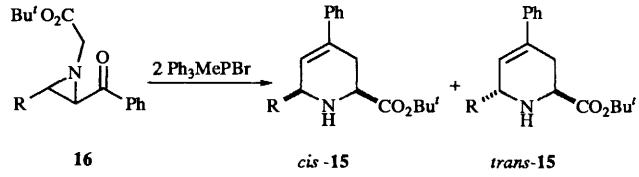
The stereochemical outcome was surprising as the aziridine **13b** exists as a 1 : 1 mixture of the *trans* and *cis* isomers. It appears likely that the aziridine *trans*-**13b** rearranges exclusively to the piperidine *cis*-**15b** (*vide infra*). The aziridine *cis*-**13b** must also rearrange to give at least some of the piperidine *cis*-**15b**. Åhman *et al.*[6] have found that a related aziridine with *cis* stereochemistry rearranged to a mixture of *cis* and *trans* piperidines, although we observed no piperidine *trans*-**15b**, R = Me. The aziridine **13a**, R = Ph gave decomposed material using base- or Lewis acid-mediated conditions.

Alkylation of the keto aziridines **11a–d**† with *tert*-butyl bromoacetate gave the aziridines **16a–d** (54–64%). (Scheme 7)‡




**Scheme 7**

We had expected that Wittig olefination of **16** would result in the formation of the vinylaziridines **13**. Using the same olefination conditions as used for the preparation of the vinylaziridines **12** (two equivalents $Ph_3MePBr$, NaH, DMSO) or using two equivalents of the phosphonium salt $Ph_3MePBr$ in DME (deprotonation by BuLi), resulted in the formation of the piperidine products **15b–d** with no vinylaziridines **13** (Scheme 8)




**Scheme 8**

(Table 2). The Wittig reagent must be effecting both the olefination of **16** and the deprotonation to the enolate needed for the rearrangement. This two step, one-pot tandem Wittig olefination–aza-Wittig rearrangement avoids the isolation of the unstable vinylaziridines and allows the synthesis of a range of piperidines, including **15c,d** (R = Bu, $Pr^i$) which were not accessible *via* the vinylaziridines **13c,d**.

It is interesting to note that the use of dimethoxyethane as the solvent at 0 °C or at room temperature results in the formation of only the piperidine *cis*-**15**, with no piperidine *trans*-**15** being observed. The preferred conformation for the [2,3]sigmatropic rearrangement must be one which has the *tert*-butyl ester group *cis* to the R group as depicted in Fig. 1. For a successful rearrangement, the vinyl group must be *cis* to the *tert*-butyl acetate group and be oriented in such a way as to allow formation of the *cis* alkene within the forming six-membered ring (a boat-shaped transition state, including all atoms of the aziridine). In this orientation, the ester group prefers to sit *endo* to the five-membered ring transition state,[17] so avoiding steric interaction with $H^a$ and allowing coordination of the lithium atom to the nitrogen atom.

When the Wittig olefination–aza-Wittig rearrangement was performed in DME at 40 °C or in DMSO then some piperidine *trans*-**15d** was isolated. The *trans* isomer must arise either when the ester group sits in the alternative orientation, or by a different mechanism, for example, involving radical intermediates, akin to the 1,2-Wittig rearrangement. This type of

† The ketone **11e** did not undergo N-alkylation, presumably for steric reasons.

‡ We have since found that the use of freshly-distilled *tert*-butyl bromoacetate improves the yield of the alkylation of N-unsubstituted aziridines.

**Table 2** Tandem olefination-aza-Wittig rearrangement of aziridine **16**

| Aziridine | R | Conditions | Yield (%) | *cis*:*trans* |
|---|---|---|---|---|
| **16a** | Ph | NaH, DMSO, 0 °C | — | — |
| **16b** | Me | BuLi, DME, r.t. | 57 | 100:0 |
| **16c** | Bu | BuLi, DME, r.t. | 55 | 100:0 |
| **16d** | Pr$^i$ | BuLi, DME, r.t. | 66 | 100:0 |
| **16d** | Pr$^i$ | BuLi, DME, 0 °C | 50 | 100:0 |
| **16d** | Pr$^i$ | BuLi, DME, 40 °C | 33 | 71:29 |
| **16d** | Pr$^i$ | NaH, DMSO, 0 °C | 31 | 58:42 |

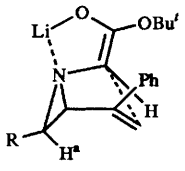



**Fig. 1**

mechanism has been postulated for the rearrangement of 2,3-*cis*-disubstituted aziridines.[6]

In summary, a number of routes to 2-vinylaziridines have been investigated. Precursor N-alkylated 2-benzoylaziridines can be prepared in just three steps from α,β-unsaturated phenyl ketones and on olefination give, not the vinylaziridines, but the ring-expanded unsaturated 4-phenylpiperidines by a [2,3]-aza-Wittig rearrangement. This chemistry has potential for the synthesis of piperidine-containing natural products and other biologically-active six-membered cyclic amines.

## Experimental

Infrared spectra were recorded on a Perkin-Elmer 881 spectrophotometer, using a polystyrene reference (1602 cm$^{-1}$). $^1$H nuclear magnetic resonance (NMR) spectra were run on a Bruker AM250 (250 MHz) or AM300 (300 MHz) instrument, with tetramethylsilane (TMS) as the reference. *J* Values are given in Hz. $^{13}$C NMR were run on a Bruker AM250 (62.9 MHz) or AM300 (75.5 MHz) instrument. Mass spectra were run on a Kratos Profile instrument. Microanalyses were carried out by Butterworth Microanalytical Consultancy Ltd., Teddington, Middlesex.

### (2*RS*,3*RS*)-3-Hydroxy-2-phenylazetidine 8

Triphenylphosphine (2.98 g, 11.27 mmol) was added to the β-azido alcohol **6**[10] (2.08 g, 10.77 mmol) in acetonitrile (45 cm$^3$) under nitrogen at room temperature. The mixture was refluxed for 6 h and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with hexane–ethyl acetate (1:4) to remove any unchanged triphenylphosphine and then $CH_2Cl_2$–ethanol (20:1) to give the *aziridine* **7**[18] (807 mg, 50%) and the *azetidine* **8** (162 mg, 10%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 3382 (OH), 3316 (NH), 1602 and 1491 (Ph); $\delta_H(CDCl_3)$ 7.50–7.25 (5 H, m, Ph), 4.12 (1 H, d, *J* 4, PhC*H*), 3.14 (1 H, ddd, *J* 4, 4 and 2.5, C*H*CH$_2$), 2.86 (1 H, dd, *J* 5 and 2.5, CHC*H*$^A$H$^B$), 2.74 (1 H, dd, *J* 5 and 4, CHCH$^A$*H*$^B$) and 1.66 (2 H, br s, NH and OH); $\delta_C(CDCl_3)$ 141.63, 128.58, 127.75, 127.03, 55.78, 55.21 and 44.15 (Found: M$^+$, 149.0840. $C_9H_{11}NO$ requires *M*, 149.0841); *m*/*z* 149 (1.4%, M) and 106 (100, M − $C_2H_3O$).

### 3-(Methoxyamino)-1-phenylbutan-1-one 10b

Methoxylamine hydrochloride (1.80 g, 21.1 mmol) was added to the alkene **9b** (2.68 g, 18.4 mmol) and triethylamine (2.9 cm$^3$, 21.0 mmol) in methanol (25 cm$^3$) at 30 °C. The mixture was heated at 50 °C for 2 h, then water (20 cm$^3$) and $CH_2Cl_2$ (20 cm$^3$) were added and the organic layer was separated. The aqueous phase was further extracted with $CH_2Cl_2$ (2 × 20 cm$^3$). The combined organic extracts were washed with brine (20 cm$^3$), dried (anhydrous $MgSO_4$), filtered and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:5) to give the *ketone* **10b** (2.89 g, 82%) as an oil, $R_f$ 0.16 (hexane–ethyl acetate, 5:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 2813 (OMe), 1680 (C=O), 1598 and 1581 (Ph); $\delta_H(CDCl_3)$ 7.97–7.88 (2 H, m, Ph), 7.55–7.37 (3 H, m, Ph), 6.84 (1 H, br s, NH), 3.63 (1 H, sextet, *J* 6.5, CH), 3.48 (3 H, s, $OCH_3$), 3.26 (1 H, dd, *J* 17 and 6.5, COC*H*$^A$H$^B$), 2.88 (1 H, dd, *J* 17 and 6.5, COCH$^A$*H*$^B$) and 1.16 (3 H, d, *J* 6.5, CHC*H*$_3$); $\delta_C(CDCl_3)$ 199.17 (C=O), 137.24 (C), 133.01 (CH), 128.53 (CH), 128.02 (CH), 62.24 ($OCH_3$), 52.55 (*C*HCH$_3$), 42.48 ($CH_2$) and 18.17 (CH*C*H$_3$) (Found: M$^+$, 193.1100. $C_{11}H_{15}NO_2$ requires *M*, 193.1103); *m*/*z* 193 (0.2%, M), 105 (100, PhCO) and 77 (37.2, Ph).

### 3-(Methoxyamino)-1-phenylheptan-1-one 10c

In the same way as for ketone **10b**, methoxylamine hydrochloride (3.0 g, 38.0 mmol), alkene **9c** (6.90 g, 37.0 mmol) and triethylamine (5.0 ml, 36.2 mmol) in methanol (60 cm$^3$) gave, after purification by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:10) the *ketone* **10c** (6.16 g, 71%) as an oil, $R_f$ 0.58 (hexane–ethyl acetate, 10:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 2810 (OMe), 1682 (C=O), 1598 and 1581 (Ph); $\delta_H(CDCl_3)$ 8.00–7.92 (2 H, m, Ph), 7.61–7.39 (3 H, m, Ph), 5.92 (1 H, br s, NH), 3.52–3.45 (1 H, m, C*H*NH), 3.47 (3 H, s, $OCH_3$), 3.28 (1 H, dd, *J* 16 and 7, COC*H*$^A$H$^B$), 2.95 (1 H, dd, *J* 16 and 5, COCH$^A$*H*$^B$), 1.71–1.16 [6 H, m, (C*H*$_2$)$_3$CH$_3$] and 0.92 (3 H, t, *J* 7, CH$_2$C*H*$_3$); $\delta_C(CDCl_3)$ 199.62 (C=O), 137.28 (C), 132.98 (CH), 128.53 (CH), 128.03 (CH), 62.04 ($OCH_3$), 57.06 (CHNH), 40.73 ($CH_2$), 31.92 ($CH_2$), 28.37 ($CH_2$), 22.76 ($CH_2$) and 13.97 ($CH_3$) (Found: M$^+$, 235.1570. $C_{14}H_{21}NO_2$ requires *M*, 235.1572); *m*/*z* 235 (3.5%, M), 204 (49.8, M − OMe), 178 (12.3, M − $C_4H_9$) and 105 (PhCO).

### 3-(Methoxyamino)-4-methyl-1-phenylpentan-1-one 10d

In the same way as for ketone **10b**, methoxylamine hydrochloride (1.415 g, 16.95 mmol), alkene **9d** (2.95 g, 16.99 mmol) and triethylamine (2.35 cm$^3$, 17 mmol) in methanol (60 cm$^3$) gave, after purification by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:8) the *ketone* **10d** (3.17 g, 84%) as an oil, $R_f$ 0.30 (hexane–ethyl acetate, 5:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 2812 (OMe), 1678 C=O), 1598 and 1581 (Ph); $\delta_H(CDCl_3)$ 8.00–7.92 (2 H, m, Ph), 7.60–7.37 (3 H, m, Ph), 5.89 (1 H, s, NH), 3.45 (3 H, s, $OCH_3$), 3.35 (1 H, ddd, *J* 8, 7 and 4, NHC*H*), 3.13 (1 H, dd, *J* 16 and 8, COC*H*$^A$H$^B$), 2.96 (1 H, dd, *J* 16 and 4, COCH$^A$*H*$^B$), 1.99 [1 H, octet, *J* 7, CH(C*H*$_3$)$_2$], 1.01 (3 H, d, *J* 7, C$^A$H$_3$) and 0.98 (3 H, d, *J* 7, C$^B$H$_3$); $\delta_C(CDCl_3)$ 199.89 (C=O), 137.47 (C), 132.89 (CH), 128.53 (CH), 128.05 (CH), 62.13 ($OCH_3$), 61.70 (CHN), 37.41 ($CH_2$), 29.25 (CHMe$_2$), 19.25 ($CH_3$) and 18.51 ($CH_3$) (Found: M$^+$, 221.1410. $C_{13}H_{19}NO_2$ requires *M*, 221.1416); *m*/*z* 221 (0.9%, M), 105 (30.2, PhCO) and 57 (100).

### 3-(Methoxyamino)-4,4-dimethyl-1-phenylpentan-1-one 10e

In the same way as for ketone **10b**, methoxylamine hydrochloride (6.40 g, 76.66 mmol), alkene **9e** (8.0 g, 42.5 mmol) and triethylamine (11.0 cm$^3$, 80 mmol) in methanol (40 cm$^3$) gave, after purification by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:8) the *ketone* **10e** (1.28 g, 13%) as an oil, $R_f$ 0.40 (hexane–ethyl acetate, 5:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 2810 (OMe), 1680 (C=O), 1598 and 1581 (Ph); $\delta_H(CDCl_3)$ 8.00–7.92 (2 H, m, Ph), 7.47–7.38 (3 H, m, Ph), 5.72 (1 H, br s, NH), 3.34 (1 H, dd, *J* 8 and 4, NHC*H*), 3.31 (3 H, s, $OCH_3$), 3.22 (1 H, dd, *J* 16 and 8,

COC*H*$^A$H$^B$), 2.92 (1 H, dd, *J* 16 and 4, COCH$^A$*H*$^B$), 1.02 [9 H, s, $(CH_3)_3$]; $\delta_C$($CDCl_3$) 197.35 (C=O), 135.02 (C), 130.00 (CH), 125.82 (CH), 125.38 (CH), 62.52 ($OCH_3$), 58.33 (CHN), 34.87 ($CH_2$), 31.06 (C) and 24.63 ($CH_3$) (Found: $M^+$, 235.1570. $C_{14}H_{21}NO_2$ requires *M*, 235.1572); *m/z* 235 (3.5%, M), 204 (50, M − OMe), 178 (12, M − $C_4H_9$) and 105 (100, PhCO).

### *trans*-2-Benzoyl-3-butylaziridine 11c

Sodium methoxide (1.8 $cm^3$, 51 mmol) was added dropwise to the methoxylamine **10c** (5.88 g, 25 mmol) in methanol (70 $cm^3$) under argon at room temperature. The reaction was heated to 50 °C for 8 h, then water (40 $cm^3$) was added and the mixture extracted with $CH_2Cl_2$ (3 × 70 $cm^3$). The combined organic extracts were washed with brine (10 $cm^3$), dried (anhydrous $MgSO_4$), filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:10) to give the *aziridine* **11c** (2.5 g, 49%) as an oil, $R_f$ 0.15 (hexane–ethyl acetate, 3:1); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 3269 (NH), 1667 (C=O), 1598, 1580 and 1493 (Ph); $\delta_H$($CDCl_3$) 8.10–7.90 (2 H, m, Ph), 7.60–7.40 (3 H, m, Ph), 3.21 (1 H, br s, COCH), 2.21–2.08 (2 H, m, NH and NC*H*Bu), 1.71–1.18 [6 H, m, $(CH_2)_3$] and 0.92 (3 H, t, *J* 7, $CH_2CH_3$); $\delta_C$($CDCl_3$) 197.13 (C=O), 136.17 (C), 133.51 (CH), 128.71 (CH), 128.09 (CH), 43.24 (CH), 39.73 (CH), 32.98 ($CH_2$), 29.29 ($CH_2$), 22.40 ($CH_2$) and 13.91 ($CH_3$) (Found: $M^+$, 203.1312. $C_{13}H_{17}NO$ requires *M*, 203.1310); *m/z* 203 (1.2%, M), 146 (44, M − $C_4H_9$), 105 (63, PhCO) and 77 (100, Ph).

### *trans*-2-Benzoyl-3-isopropyl aziridine 11d

In the same way as for aziridine **11c**, sodium methoxide (4.4 $cm^3$, 29.84 mmol) and the methoxylamine **10d** (3.17 g, 14.33 mmol) in methanol (60 $cm^3$) gave, after 5 h at 50 °C and purification by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:5) the *aziridine* **11d** (2.210 g, 82%) as an oil, $R_f$ 0.15 (hexane–ethyl acetate, 5:1); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 3274 (NH), 1666 (C=O), 1598 and 1581 (Ph); $\delta_H$($CDCl_3$) 8.07–7.97 (2 H, m, Ph), 7.65–7.43 (3 H, m, Ph), 3.29 (1 H, br s, COCH), 2.08 (1 H, br s, NH), 1.97 (1 H, br d, *J* 7, CHC*H*CH), 1.50 (1 H, octet, *J* 7, C*H*$Me_2$), 1.07 (3 H, d, *J* 7, C$^A$$H_3$) and 1.03 (3 H, d, *J* 7, C$^B$$H_3$); $\delta_C$($CDCl_3$) 197.19 (CO), 136.15 (C), 133.54 (CH), 128.75 (CH), 128.09 (CH), 49.72 (*C*HCO), 38.96 (CH*C*HCH), 32.03 (*C*H$Me_2$), 20.18 ($CH_3$) and 19.62 ($CH_3$) (Found: $M^+$, 189.1155. $C_{12}H_{15}NO$ requires *M*, 189.1154); *m/z* 189 (1.0%, M), 146 (100, M − $C_3H_7$), 105 (55.2, PhCO) and 77 (37.7, Ph).

### *trans*-2-Benzoyl-3-*tert*-butyl 11e

In the same way as for aziridine **11c**, sodium methoxide (0.93 $cm^3$, 6.31 mmol) and the methoxylamine **10e** (1.8 g, 8.16 mmol) in methanol (10 $cm^3$) gave, after 48 h at 50 °C and purification by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:10) the *aziridine* **11e** (0.60 g, 36%) as an oil, $R_f$ 0.28 (hexane–ethyl acetate, 10:1); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 3276 (NH), 1667 (C=O), 1598 and 1581 (Ph); $\delta_H$($CDCl_3$) 8.05–7.97 (2 H, m, Ph), 7.64–7.47 (3 H, m, Ph), 3.34 (1 H, m, NH), 2.05 (2 H, m, CHCHN) and 0.98 [9 H, s, $(CH_3)_3$]; $\delta_C$($CDCl_3$) 195.03 (CO), 133.52 (C), 130.89 (CH), 126.13 (CH), 125.44 (CH), 49.99 (CHN), 34.12 (CH), 28.63 (C) and 24.12 ($CH_3$).

### *trans*-2-butyl-3-(1-phenylvinyl)aziridine 12c

Butyllithium (2.5 mol $dm^{-3}$ in hexane; 1.98 $cm^3$, 4.95 mmol) was added to methyl(triphenyl)phosphonium bromide (1.78 g, 4.93 mmol) in 1,2-dimethoxyethane (DME) (15 $cm^3$) under nitrogen at room temperature. After 20 min the ketone **11c** (0.5 g, 2.46 mmol) in DME (5 $cm^3$) was added and the mixture was stirred for 6 h. Water (20 $cm^3$) was added and the mixture extracted with $CH_2Cl_2$ (3 × 20 $cm^3$). The organic extracts were dried (anhydrous $MgSO_4$), filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:3) to give the *vinyl aziridine* **12c** (0.40 g, 81%), $R_f$ 0.15 (hexane-ethyl acetate, 2:1); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 3269 (NH), 1672 (C=C), 1626 (NH bend), 1598, 1574 and 1494 (Ph); $\delta_H$($CDCl_3$) 7.53–7.45 (2 H, m, Ph), 7.38–7.26 (3 H, m, Ph), 5.36 (1 H, s, C=C*H*$^A$H$^B$), 5.17 (1 H, br s, C=CH$^A$*H*$^B$), 2.49 (1 H, d, *J* 3, CC*H*NH), 1.94–1.88 (1 H, m, C*H*$CH_2$), 1.72–1.33 [7 H, m, $(CH_2)_3$ and NH] and 0.92 (3 H, t, *J* 7, $CH_2CH_3$); $\delta_C$($CDCl_3$) 147.27 (*C*=$CH_2$), 139.64 (C), 128.33 (CH), 127.80 (CH), 126.23 (CH), 110.57 (C=*C*$H_2$), 40.29 (CH), 39.76 (CH), 33.95 ($CH_2$), 29.64 ($CH_2$), 22.55 ($CH_2$) and 14.00 ($CH_3$) (Found: $M^+$, 201.1523. $C_{14}H_{19}N$ requires *M*, 201.1517); *m/z* 201 (20.6%, M), 158 (19.6, M − $C_3H_7$) and 144 (100, M − $C_4H_9$).

### *trans*-2-Isopropyl-3-(1-phenylvinyl)aziridine 12d

Sodium hydride (60% dispersion in oil; 300 mg, 7.5 mmol) was washed with hexane (2 × 6 $cm^3$). Dry dimethyl sulfoxide (DMSO) (20 $cm^3$) was added and the mixture heated to 70 °C for 45 min, before being cooled to 0 °C. Methyl(triphenyl)phosphine bromide (2.672 g, 7.5 mmol) in DMSO (10 $cm^3$) was added dropwise and the mixture was stirred at room temperature for 30 min before the ketone **11d** (550 mg, 2.91 mmol) in DMSO (10 $cm^3$) was added. After 30 min, water (50 $cm^3$) was added and the mixture was extracted with diethyl ether (3 × 30 $cm^3$). The combined organic extracts were washed with brine (30 $cm^3$), dried (anhydrous $MgSO_4$), filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:4) to give the *alkene* **12d** (363 mg, 67%) as an oil, $R_f$ 0.25 (hexane–ethyl acetate, 4:1); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 3303 (NH), 1625 (C=C), 1599, 1573 and 1492 (Ph); $\delta_H$($CDCl_3$) 7.59–7.47 (2 H, m, Ph), 7.43–7.26 (3 H, m, Ph), 5.35 (1 H, s, C=C*H*$^A$H$^B$), 5.18 (1 H, s, C=CH$^A$*H*$^B$), 2.56 (1 H, d, *J* 3, CCH), 1.75 (1 H, dd, *J* 7 and 3, CHC*H*CH), 1.41 (1 H, octet, *J* 7, C*H*$Me_2$), 1.09 (1 H, d, *J* 7, C$^A$$H_3$) and 1.06 (1 H, d, *J* 7, C$^B$$H_3$); $\delta_C$($CDCl_3$) 147.50 (*C*=$CH_2$), 139.83 (C), 128.31 (CH), 127.77 (CH), 126.36 (CH), 110.78 ($CH_2$), 46.78 (CH), 39.04 (CH), 32.70 ($CHMe_2$), 20.20 ($CH_3$) and 20.10 ($CH_3$) (Found: $M^+$, 187.1352. $C_{13}H_{17}N$ requires *M*, 187.1361); *m/z* 187 (5%, M), 144 (30.4, M − $C_3H_7$) and 57 (100).

### (2′*RS*,3′*RS*)-*tert*-Butyl 2-[2′-phenyl-3-(1-phenylvinyl)aziridin-1-yl]acetate 13a

*tert*-Butyl bromoacetate (0.44 $cm^3$, 2.68 mmol) was added dropwise to the aziridine **12a** (512 mg, 2.32 mmol) and potassium carbonate (64 mg, 0.46 mmol) in acetonitrile (8 $cm^3$) under argon at room temperature followed by the addition of further potassium carbonate (360 mg, 2.60 mmol). After 37 h, water (20 $cm^3$) was added and the mixture extracted with $CH_2Cl_2$ (3 × 15 $cm^3$). The combined organic extracts were washed with brine (15 $cm^3$), dried (anhydrous $MgSO_4$), filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–hexane (1:8) to give the *aziridine* **13a** (390 mg, 50%) as an oil, $R_f$ 0.42 (hexane–ethyl acetate, 4:1); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1736 (C=O), 1599 and 1492 (Ph); $\delta_H$($CDCl_3$) 7.71–7.22 (10 H, m, Ph), 5.97–5.35 (2 H, br m, $CCH_2$), 3.45–2.87 (4 H, br m, PhC*H*C*H* and $NCH_2$) and 1.38 [9 H, s, $C(CH_3)_3$] (Found: $M^+$, 335.1882. $C_{22}H_{25}NO_2$ requires *M*, 335.1885); *m/z* 335 (1.6%, M), 278 (7.3, M − Bu$^t$) and 91 (100).

**(2'*RS*,3'*RS*)- and (2'*RS*,3'*R*)-*tert*-Butyl 2-[2'-methyl-3'-(1-phenylvinyl)aziridin-1-yl]acetate 13b** In the same way as for the aziridine **13a**, *tert*-butyl bromoacetate (0.27 $cm^3$, 1.62 mmol), the aziridine **12b** (242 mg, 1.5 mmol) and potassium carbonate (416 mg, 3.04 mmol) in acetonitrile (8 $cm^3$), gave, after purification by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:4), the *aziridine* **13b** (200 mg, 48%) as a mixture (1:1) of *cis* and *trans* diastereoisomers as an oil, $R_f$ 0.34 (hexane–ethyl acetate, 4:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 1735 (C=O), 1672 (C=C), 1600, 1574 and 1494 (Ph); $\delta_H(CDCl_3)$ 7.62–7.24 (10 H, m, Ph), 5.82 (1 H, s, C=CH), 5.49 (1 H, s, C=CH), 5.41 (1 H, s, C=CH), 5.17 (1 H, s, C=CH), 3.38 (1 H, d, *J* 16, $CH^AH^B$), 3.26 (1 H, d, *J* 16, $CH^AH^B$), 3.18 (1 H, d, *J* 16, $CH^AH^B$), 2.80–2.73 (1 H, m, CHCHMe), 2.66 (1 H, d, *J* 16, $CH^AH^B$), 2.16–2.03 (2 H, m, CHCHMe), 1.97–1.89 (1 H, m, CHMe) and 1.54–1.38 [24 H, m, 2 × Me and 2 × $C(CH_3)_3$]; $\delta_C(CDCl_3)$ 170.52 and 170.14 (C=O), 145.47 and 140.88 (C), 139.75 and 139.24 (C), 128.51 and 128.31 (CH), 128.22 and 128.09 (CH), 127.56 and 125.84 (CH), 116.46 and 111.90 ($CH_2$), 81.02 and 80.84 (C), 54.32 and 54.05 ($CH_2$), 48.98 and 47.06 (CH), 40.74 and 39.78 (CH), 28.09 [2 × $C(CH_3)_3$], 18.08 and 11.31 ($CH_3$) (Found: $M^+$, 273.1723. $C_{17}H_{23}NO_2$ requires *M*, 273.1728); *m/z* 273 (16.6%, M), 258 (9, M − Me), 217 (100, M − Bu$^t$), 202 (79, M − Me − Bu$^t$), 172 (95, M − $CO_2Bu^t$) and 145 (96).

**(2*RS*,6*RS*)-*tert*-Butyl 6-methyl-4-phenyl-1,2,3,6-tetrahydropyridine-2-carboxylate *cis*-15b**

**Method A.** Butyllithium (0.32 $cm^3$, 0.80 mmol) was added to diisopropylamine (0.12 $cm^3$, 0.91 mmol) in tetrahydrofuran (THF) (5 $cm^3$) at 0 °C under argon. After 1 h, the mixture was cooled to −78 °C and the aziridine **13a** (160 mg, 0.59 mmol) in THF (5 $cm^3$) was added dropwise. After 5 min, water (5 $cm^3$) was added and the mixture was allowed to warm to room temperature and extracted with $CH_2Cl_2$ (3 × 20 $cm^3$). The combined organic extracts were washed with brine (20 $cm^3$), dried (anhydrous $MgSO_4$), filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:2) to give *tetrahydropyridine cis*-**15b** (101 mg, 63%) as an oil, $R_f$ 0.22 (hexane–ethyl acetate, 3:2); $\nu_{max}(CHCl_3)/cm^{-1}$ 3335 (NH), 1725 (C=O), 1644 (C=C), 1600, 1577 and 1494 (Ph); $\delta_H(CDCl_3)$ 7.31–7.21 (5 H, m, Ph), 5.97–5.94 (1 H, m, =CH), 3.72–3.62 (1 H, m, CHMe), 3.61 (1 H, dd, *J* 11 and 4.5, CHCO), 2.68 (1 H, dddd, *J* 16.5, 4, 3 and 1, $CH^AH^B$), 2.52 (1 H, dddd, *J* 16.5, 11, 4 and 2.5, $CH^AH^B$), 2.05 (1 H, br s, NH), 1.50 [9 H, s, $C(CH_3)_3$] and 1.28 (3 H, d, *J* 7, $CHCH_3$); $\delta_C(CDCl_3)$ 172.30 (C=O), 140.86 (C=CH), 134.34 (C), 128.89 (CH), 127.21 (CH), 125.13 (CH), 81.35 ($CMe_3$), 56.76 (CH), 50.44 (CH), 30.68 ($CH_2$), 28.07 [$C(CH_3)_3$] and 22.03 ($CHCH_3$) (Found: $M^+$, 273.1729. $C_{17}H_{23}NO_2$ requires *M*, 273.1729); *m/z* 273 (8.1%, M), 216 (14.8, M − Bu$^t$) and 172 (100, M − $CO_2Bu^t$).

**Method B.** Butyllithium (2.5 mol $dm^{-3}$ in hexanes; 0.44 $cm^3$, 1.10 mmol) was added dropwise to methyl(triphenyl)-phosphonium bromide (435 mg, 1.22 mmol) in DME (8 $cm^3$) under nitrogen at room temperature. After 15 min the mixture was transferred by cannula to the aziridine **16b** (140 mg, 0.52 mmol) in DME (4 $cm^3$). After 30 min, water (20 $cm^3$) was added and the mixture extracted with $CH_2Cl_2$ (3 × 20 $cm^3$). The combined organic extracts were washed with brine (20 $cm^3$), dried (anhydrous $MgSO_4$), filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:2) to give tetrahydropyridine *cis*-**15b** (80 mg, 57%) as an oil, data as above.

**(2*RS*,6*RS*)-*tert*-Butyl 6-butyl-4-phenyl-1,2,3,6-tetrahydropyridine-2-carboxylate *cis*-15c**

In the same way as for the tetrahydropyridine *cis*-**15b**, method B, butyllithium (2.5 mol $dm^{-3}$ in hexane, 0.28 $cm^3$, 0.70 mmol), methyl(triphenyl)phosphonium bromide (269 mg, 0.75 mmol) in DME (4 $cm^3$) and the aziridine **16c** (96 mg, 0.30 mmol) in DME (2 $cm^3$) gave, after purification by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:7) the *tetrahydropyridine cis*-**15c** (52 mg, 55%) as an oil, $R_f$ 0.38 (hexane–ethyl acetate, 5:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 3339 (NH), 1727 (C=O), 1599 and 1493 (Ph); $\delta_H(CDCl_3)$ 7.37–7.16 (5 H, m, Ph), 6.00 (1 H, br s, =CH), 3.58 (1 H, dd, *J* 10.5 and 4.5, CHCO), 3.57–3.48 (1 H, m, $CHCH_2$), 2.74–2.44 (2 H, m, $CCH_2$), 2.00 (1 H, br s, NH), 1.70–1.31 [6 H, m, $(CH_2)_3$], 1.54 [9 H, s, $C(CH_3)_3$] and 0.92 (3 H, t, *J* 7, $CH_2CH_3$); $\delta_C(CDCl_3)$ 172.50 (C=O), 141.20 (C=CH), 134.73 (C), 128.40 (CH), 127.98 (CH), 127.22 (CH), 125.25 (CH), 81.32 ($CMe_3$), 56.77 (CH), 55.04 (CH), 36.23 ($CH_2$), 31.18 ($CH_2$), 28.12 [$C(CH_3)_3$], 28.01 ($CH_2$), 22.85 ($CH_2$) and 13.98 ($CH_3$) (Found: $M^+$, 315.2209. $C_{20}H_{29}NO_2$ requires *M*, 315.2209); *m/z* 315 (10.8%, M), 258 (33.1, M − Bu$^t$) and 83 (100).

**(2*RS*,6*RS*)-*tert*-Butyl 6-isopropyl-4-phenyl-1,2,3,6-tetrahydropyridine-2-carboxylate *cis*-15d**

In the same way as for the tetrahydropyridine *cis*-**15b**, method B, butyllithium (1.8 mol $dm^{-3}$ in hexane; 0.70 $cm^3$, 1.26 mmol), methyl(triphenyl)phosphonium bromide (460 mg, 1.29 mmol) in DME (8 $cm^3$) and the aziridine **16d** (182 mg, 0.60 mmol) in DME (4 $cm^3$) gave, after purification by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:8) the *tetrahydropyridine cis*-**15d** (119 mg, 66%) as an oil, $R_f$ 0.35 (hexane–ethyl acetate, 5:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 3351 (NH), 1724 (C=O), 1598 and 1494 (Ph); $\delta_H(CDCl_3)$ 7.42–7.21 (5 H, m, Ph), 6.04–6.01 (1 H, m, =CH), 3.58 (1 H, dd, *J* 16 and 4, CHCO), 3.42–3.36 (1 H, m, $CHPr^i$), 2.69 (1 H, dddd, *J* 16, 4, 3 and 0.5, $CH^AH^B$), 2.52 (1 H, dddd, *J* 16, 11, 4 and 2, $CH^AH^B$), 2.12 (1 H, br s, NH), 1.90–1.78 (1 H, m, $CHMe_2$), 1.50 [9 H, s, $C(CH_3)_3$], 1.03 (3 H, d, *J* 7, $CHC^AH_3$) and 1.02 (3 H, d, *J* 7, $CHC^BH_3$); $\delta_C(CDCl_3)$ 172.53 (C=O), 141.25 (C=CH), 135.58 (C), 128.32 (CH), 127.12 (CH), 126.13 (CH), 125.16 (CH), 81.26 ($CMe_3$), 60.60 (CH), 56.74 (CH), 33.01 ($CHMe_2$), 31.26 ($CH_2$), 28.11 [$C(CH_3)_3$], 18.52 ($CH_3$) and 18.47 ($CH_3$) (Found: $M^+$, 301.2043. $C_{19}H_{27}NO_2$ requires *M*, 301.2042); *m/z* 301 (1.5%, M), 258 (32.9, M − $C_3H_7$) and 84 (100).

**(2*RS*,6*SR*)-*tert*-Butyl 6-isopropyl-4-phenyl-1,2,3,6-tetrahydropyridine-2-carboxylate *trans*-15d**

Sodium hydride (95 mg, 2.38 mmol), washed with hexane and dry DMSO (15 $cm^3$) were heated to 65 °C for 45 min. The mixture was then cooled to 0 °C and methyl(triphenyl)phosphonium bromide (890 mg, 2.5 mmol) in DMSO (8 $cm^3$) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 30 min. The ketone **16d** (310 mg, 1.02 mmol) in DMSO (4 $cm^3$) was added dropwise at room temperature. After 90 min, water (30 $cm^3$) was added and the mixture extracted with diethyl ether (3 × 30 $cm^3$). The combined organic extracts were washed with brine (30 $cm^3$), dried (anhydrous $MgSO_4$), filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:8) to give the tetrahydropyridine *cis*-**15d** (55 mg, 18%) as an oil, data as above and the *tetrahydropyridine trans*-**15d** (40 mg, 13%) as an oil, $R_f$ 0.24 (hexane–ethyl acetate, 5:1); $\nu_{max}(CHCl_3)/cm^{-1}$ 3362 (NH), 1721 (C=O), 1599 and 1495 (Ph); $\delta_H(CDCl_3)$ 7.43–7.18 (5 H, m, Ph), 6.03–5.98 (1 H, m, =CH), 3.79 (1 H, t, *J* 5, CHCO),

3.46 (1 H, td, *J* 5 and 3, C*H*Pr$^i$), 2.85–2.65 (2 H, m, $CH_2$), 2.38 (1 H, br s, NH), 1.78 (1 H, octet, *J* 7, C*H*Me$_2$), 1.48 [9 H, s, C(C$H_3$)$_3$], 1.02 (3 H, d, *J* 7, CHC$^A$*H*$_3$) and 1.00 (3 H, d, *J* 7, CHC$^B$*H*$_3$); $\delta_C$($CDCl_3$) 173.21 (C=O), 141.65 (*C*=CH), 134.76 (C), 128.28 (CH), 127.00 (CH), 125.58 (CH), 125.26 (CH), 81.02 (*C*Me$_3$), 57.08 (CH), 54.22 (CH), 33.48 (*C*HMe$_2$), 29.59 ($CH_2$), 28.09 [C(*C*H$_3$)$_3$], 19.04 ($CH_3$) and 18.65 ($CH_3$) (Found: M$^+$, 301.2049. $C_{19}H_{27}NO_2$ requires *M*, 301.2042); *m*/*z* 301 (2.3%, M), 258 (27.4, M − $C_3H_7$) and 202 (100, M − $C_7H_{15}$).

**(2′*RS*,3′*SR*)-*tert*-Butyl 2-(2′-benzoyl-3′-phenylaziridin-l-yl)-acetate 16a**

*tert*-Butyl bromoacetate (1.0 cm$^3$, 6.09 mmol) was added dropwise to the aziridine **11a** (1.11 g, 4.97 mmol), 18-crown-6 (35 mg) and potassium carbonate (1.41 g, 10.0 mmol) in acetonitrile (15 cm$^3$) under nitrogen at room temperature. The mixture was heated to 55 °C for 48 h, then water (20 cm$^3$) was added and the mixture extracted with $CH_2Cl_2$ (3 × 30 cm$^3$). The combined organic extracts were washed with brine (30 cm$^3$), dried (anhydrous $MgSO_4$), filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (1:7) to give the *aziridine* **16a** [480 mg, 29% (58% based on recovered starting material)] as a white solid, recrystallised from hexane, mp 105.0–106.0 °C; $R_f$ 0.33 (hexane–ethyl acetate, 4:1); $\nu_{max}$($CHCl_3$)/cm$^{-1}$ 1734 (C=O), 1665 (C=O), 1598, 1581 and 1494 (Ph); $\delta_H$($CDCl_3$) 8.04 (2 H, br d, *J* 7, $C_6H_2$), 7.63–7.25 (8 H, m, $C_6H_3$ and Ph), 3.86 (1 H, br d, *J* 17, NC*H*$^A$H$^B$), 3.76 (1 H, d, *J* 2.5, CHCO), 3.72 (1 H, br d, *J* 17, NCH$^A$*H*$^B$), 3.46 (1 H, br s, PhC*H*) and 1.36 [9 H, s, C(C$H_3$)$_3$]; $\delta_C$($CDCl_3$) 195.13 (C=O), 169.59 ($CO_2$), 138.30 (C), 137.94 (C), 133.32 (CH), 128.63 (CH), 128.52 (CH), 128.43 (CH), 127.71 (CH), 126.47 (CH), 81.13 (*C*Me$_3$), 52.91 ($CH_2$), 49.61 (CO*C*H), 46.85 (*C*HPh) and 27.95 [C(*C*H$_3$)$_3$] (Found: M$^+$, 337.1682. $C_{21}H_{23}NO_3$ requires *M*, 337.1678); *m*/*z* 338 (3.2%, M + H), 337 (13.5, M), 281 [(M + H) − $C_4H_9$] and 105 (98.4, PhCO) (Found: C, 74.7; H, 6.8; N, 4.2. $C_{21}H_{23}NO_3$ requires C, 74.75; H, 6.87; N, 4.15%).

**(2′*RS*,3′*SR*)-*tert*-Butyl 2-(2′-benzoyl-3′-methylaziridin-1-yl)-acetate 16b**

*tert*-Butyl bromoacetate (0.50 cm$^3$, 3.0 mmol) was added dropwise to a mixture of aziridine **11b** (362 mg, 2.25 mmol) and potassium carbonate (620 mg, 4.50 mmol) in acetonitrile (8 cm$^3$) under nitrogen at room temperature. After 24 h, water (20 cm$^3$) was added and the mixture was extracted with dichloromethane (3 × 20 cm$^3$). The combined organic extracts were washed with brine (20 cm$^3$), dried (anhydrous $MgSO_4$), filtered and the solvent evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with ethyl acetate–light petroleum (bp 40–60 °C) (2:5) to give the *aziridine* **16b** (395 mg, 64%) as a white solid, recrystallised from hexane, mp 55.0–56.0 °C; $R_f$ 0.29 (hexane–ethyl acetate, 2:1); $\nu_{max}$($CHCl_3$)/cm$^{-1}$ 1734 (C=O), 1665 (C=O), 1590 and 1580 (Ph); $\delta_H$($CDCl_3$) 8.07–7.97 (2 H, m, Ph), 7.62–7.42 (3 H, m, Ph), 3.61 (1 H, d, *J* 17, NC*H*$^A$H$^B$), 3.46 (1 H, d, *J* 17, NCH$^A$*H*$^B$), 3.43 (1 H, d, *J* 3, COCH), 2.44 (1 H, qd, *J* 5 and 3, C*H*CH$_3$), 1.37 (3 H, d, *J* 5, CHC*H*$_3$) and 1.36 [9 H, s, C(C$H_3$)$_3$]; $\delta_C$($CDCl_3$) 196.05 (CO), 169.80 ($CO_2$), 138.14 (C), 133.16 (CH), 128.57 (CH), 128.39 (CH), 80.93 (*C*Me$_3$), 52.88 ($CH_2$), 43.68 (CH), 43.63 (CH), 27.93 [C(*C*H$_3$)$_3$] and 18.00 (CH*C*H$_3$) (Found: M$^+$, 275.1511. $C_{16}H_{21}NO_3$ requires *M*, 275.1521); *m*/*z* 275 (2.6%, M), 204 (100), 174 (52.8, M − $CO_2$Bu$^t$) and 105 (100, PhCO) (Found: C, 69.8; H, 7.6; N, 5.0. $C_{16}H_{21}NO_3$ requires C, 69.79; H, 7.69; N, 5.09%).

**(2′*RS*,3′*SR*)-*tert*-Butyl 2-(2′-benzoyl-3′-butylaziridin-1-yl)acetate 16c**

In the same way as for the aziridine **16b**, *tert*-butyl bromoacetate (0.46 cm$^3$, 2.97 mmol), the aziridine **11c** (600 mg, 2.96 mmol) and potassium carbonate (0.8 g, 6.0 mmol) in acetonitrile (10 cm$^3$), gave, after 72 h, the *aziridine* **16c** (500 mg, 54%) as an oil, $R_f$ 0.34 (hexane–ethyl acetate, 5:1); $\nu_{max}$($CHCl_3$)/cm$^{-1}$ 1735 (C=O), 1665 (C=O), 1597 and 1480 (Ph); $\delta_H$($CDCl_3$) 8.03–7.95 (2 H, m, Ph), 7.53–7.45 (3 H, m, Ph), 3.52 (1 H, d, *J* 17, NC*H*$^A$H$^B$), 3.47 (1 H, d, *J* 17, NCH$^A$*H*$^B$), 3.45 (1 H, d, *J* 2, PhCOC*H*N), 2.37 (1 H, td, *J* 4 and 2, NC*H*CH$_2$), 1.70–1.25 [6 H, m, $(CH_2)_3$], 1.30 [9 H, s, $(CH_3)_3$] and 0.84 (3 H, t, *J* 7, $CH_2CH_3$); $\delta_C$($CDCl_3$) 196.12 (C=O), 169.75 (C=O), 138.77 (C), 133.10 (CH), 128.55 (CH), 128.39 (CH), 80.88 (C), 53.13 ($CH_2$), 48.63 (CH), 42.86 (CH), 32.41 ($CH_2$), 29.14 ($CH_2$), 27.89 [C(*C*H$_3$)$_3$], 22.37 ($CH_2$) and 13.92 ($CH_3$) (Found: M$^+$, 317.1990. $C_{19}H_{27}NO_3$ requires *M*, 317.2002); *m*/*z* 317 (1.3%, M), 261 (12.8, M − Bu$^t$), 105 (49, PhCO) and 77 (100, Ph).

**(2′*RS*,3′*SR*)-*tert*-Butyl 2-(2′-benzoyl-3′-isopropyl)aziridin-1-yl)-acetate 16d**

In the same way as for the aziridine **16b**, *tert*-butyl bromoacetate (0.80 cm$^3$, 4.80 mmol), the aziridine **11d** (687 mg, 3.63 mmol) and potassium carbonate (979 mg, 7.10 mmol) in acetonitrile (20 cm$^3$), gave, after 5 days, the *aziridine* **16d** (695 mg, 63%) as a white solid, recrystallised from hexane, mp 65.0–66.0 °C; $R_f$ 0.25 (hexane–ethyl acetate, 4:1); $\nu_{max}$($CHCl_3$)/cm$^{-1}$ 1736 (C=O), 1666 (C=O), 1599 and 1581 (Ph); $\delta_H$($CDCl_3$) 8.10–7.97 (2 H, m, Ph), 7.70–7.47 (3 H, m, Ph), 3.63 (1 H, d, *J* 16, NC*H*$^A$H$^B$), 3.53 (1 H, d, *J* 3, PhCOC*H*), 3.50 (1 H, d, *J*, 16, NCH$^A$*H*$^B$), 2.17 (1 H, dd, *J* 7 and 3, C*H*CHMe$_2$), 1.51 (1 H, octet, *J* 7, C*H*Me$_2$), 1.37 [9 H, s, C(C$H_3$)$_3$], 1.06 (3 H, d, *J* 7, C$^A$H$_3$) and 0.93 (3 H, d, *J* 7, C$^B$H$_3$); $\delta_C$($CDCl_3$) 196.16 (CO), 169.78 ($CO_2$), 138.20 (C), 133.10 (CH), 128.57 (CH), 128.42 (CH), 80.90 (*C*Me$_3$), 55.27 (*C*HCO), 53.47 ($CH_2$), 42.03 (*C*HCHMe$_2$), 31.71 (*C*HMe$_2$), 27.92 [C(*C*H$_3$)$_3$], 20.22 (CH*C*H$_3$) and 19.33 (CH*C*H$_3$) (Found: M$^+$, 303.1843. $C_{18}H_{25}NO_3$ requires *M*, 303.1834); *m*/*z* 303 (0.3%, M), 260 (8.6, M − $C_3H_7$), 204 (100) and 202 (11.2, M − $CO_2$Bu$^t$) (Found: C, 71.4; H, 8.25; N, 4.6. $C_{18}H_{25}NO_3$ requires C, 71.26; H, 8.31; N, 4.62%).

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