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Asymmetric aziridine synthesis by aza-Darzens reaction of *N*-diphenylphosphinylimines with chiral enolates. Part 2: Inversion of diastereoselectivity

J. B. Sweeney,[a,b,*] Alex A. Cantrill,[b] Michael G. B. Drew,[a] Andrew B. McLaren[a] and Smita Thobhani[a]

[a]*School of Chemistry, University of Reading, Reading RG1 5JN, UK*
[b]*School of Chemistry, University of Bristol, Bristol BS8 1TS, UK*

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Abstract—The aza-Darzens ('ADZ') reactions of *N*-diphenylphosphinyl ('*N*-Dpp') imines with chiral enolates derived from *N*-bromoacetyl 2*S*-2,10-camphorsultam proceed in generally good yield to give *N*-diphenylphosphinyl aziridinoyl sultams. However, the stereoselectivity of the reaction is dependent upon the structure of the imine substituent: when the chiral enolate was reacted with arylimines substituted in the *ortho*-position, mixtures of *cis*- and *trans*-2′*R*,3′*R*-aziridines were obtained, often with a complete selectivity in favour of the trans-isomer.

1. Introduction

We have recently described our studies of the aza-Darzens reaction ('ADZ') of *N*-diphenylphosphinyl ('*N*-Dpp') imines with enolates derived from *N*-bromoacetylcamphorsultam, which proceed with good efficiency and high levels of stereoselectivity.[1] In the reactions of *N*-Dpp aryl imines with these enolates, in common with other such reactions, there often is an inherent propensity for the formation of *cis*-aziridines as the major products. This is a consequence of the stepwise nature of the mechanism involved (vide infra). In this manuscript, we describe how the presence of sterically-demanding imine substitutents can invert the diastereoselectivity of the ADZ reaction, allowing for the obtention of *trans*-aziridines from this process.

2. Results and discussion

2.1. ADZ reaction of unsaturated imines

The first sign that the ADZ reaction might be tunable according to substituent pattern in the imine was observed in the reactions of α,β-unsaturated imines. Thus, in the reaction of the camphor enolate with Dpp–imine derived from acrolein, *cis*-aziridine[†] **1a** was obtained as the only product of the reaction, in moderate yield. However, when the analogous reaction was carried out using the imine from 3,3-dimethylacrolein, we obtained two products (Scheme 1). The first was **1b**, an aziridine with $^{2}J_{H}=$ 2.9 Hz, indicative of a trans-stereochemistry. The second product was a non-crystalline, non-aziridine product, tentatively identified as pyrroline (**2**, obtained in 20% yield).

The latter compound would be obtained via 1,4-addition of the chiral enolate followed by 5-*exo*-tet cyclization of the resulting amide anion. Despite many attempts, we have been unable to confirm either the gross structure or stereochemistry of the fragile by-product **2**. Given that we had previously observed only cis-configured aziridines (often the products of asymmetric aziridination reactions)[2] in these aza-Darzens reactions, we were intrigued by the observation and we postulated that the inverted stereoselectivity might be due to the extra steric demand present in the more substituted imine due to the *gem*-dimethyl substitution pattern. We set out to examine the scope of the trans-selective reaction.

2.2. ADZ reaction of *ortho*-substituted aryl imines

In the first instance, we chose a range of *ortho*-substituted aryl imines as suitable substrates to provide pertinent information about the breadth of the process. *N*-Dpp-2-chlorobenzaldimine reacted under the standard conditions to give a mixture of

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* Corresponding author. Tel.: +118 931 6585; fax: +118 378 6331; e-mail: j.b.sweeney@rdg.ac.uk

[†] Decoupling experiments indicated $J\sim 6$ Hz.

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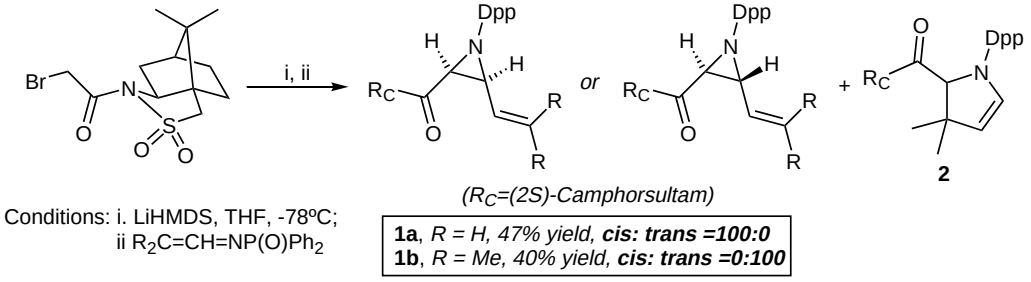
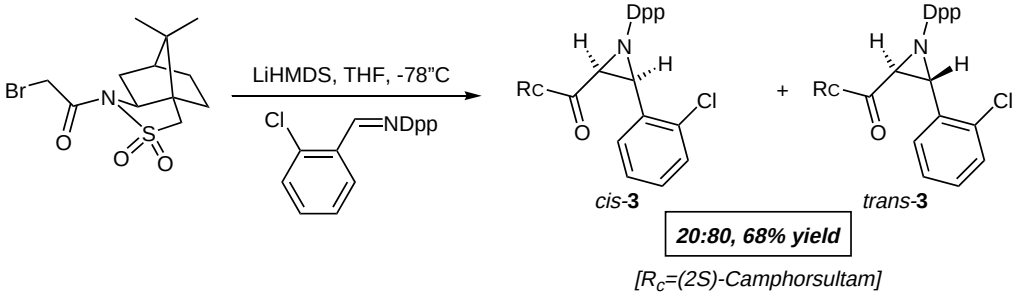
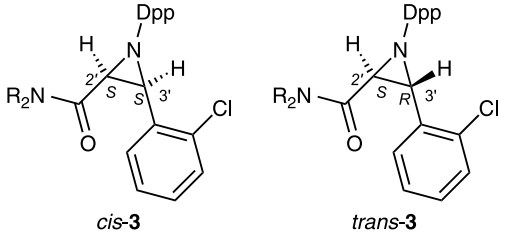


Scheme 1.



Scheme 2.



cis-isomer	64.58	52.46	48.95	47.70	44.56	40.72	40.66	32.49	38.12	26.29	20.55	19.72
trans-isomer	65.11	52.71	48.76	47.59	44.37	43.99	41.27	32.52	37.75	26.29	20.64	19.65
Δδ/ppm	0.53	0.25	-0.11	-0.11	-0.19	3.27	0.61	0.03	-0.37	0.00	0.09	-0.07

Figure 1. Selected ^{13}C NMR data for *cis*-**3** and *trans*-**3**.

cis- and *trans*-aziridines **3** (cis:trans =20:80, J=6.1, 2.8 Hz, respectively) in a combined yield of 68% (Scheme 2).

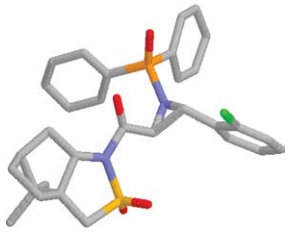
Although the obtention of a mixture of diastereoisomers, and the coupling constants shown by these products, gave a clear indication that the diastereoselectivity of the reaction had been inverted to favour the trans-isomer, *cis*-**3** and *trans*-**3** did not initially produce crystals suitable for analysis by X-ray crystallography. We were, therefore, forced to seek an alternative means to confirm the actual stereochemistry of the compounds. Although we felt it was reasonable to assume that the diastereoface selectivity of the reaction (vide infra) was unaltered (meaning that the absolute stereochemistry at C′-2 would be *S*), we were, of course, motivated to provide more compelling evidence for the stereochemistry engendered by the reaction. As a first means of assessing the compounds, we examined the ^{13}C NMR spectra of *cis*-**3** and *trans*-**3** (Fig. 1).

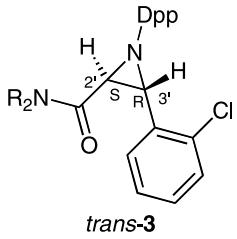
Thus, we observed that in the NMR spectra of *cis*-**3** and *trans*-**3** there was significant (≥5%) divergence in the chemical shift value of only one of the non-aromatic resonances recorded for each compound. Since we had previously demonstrated in an unambiguous manner[‡] that this resonance belonged to the benzylic aziridine carbon (i.e., position 3′), we felt confident in stating that the stereochemistry of *trans*-**3** was (2′*S*, 3′*R*), as shown in Figure 1. To our delight, when we subsequently obtained single crystals of *trans*-**3**, which were suitable for X-ray analysis, our initial stereochemical assignment was vindicated (Fig. 2).

When the reaction was repeated with a range of *ortho*-substituted aryl imines, a pattern began to emerge (Table 1).

In all but one of the ADZ reactions of *ortho*-substituted benzaldimines examined, *trans*-aziridines were observed in the product mixture and in several cases (entries 5–7, 10) the reaction provided only the trans-isomer; only in the reaction of

[‡] Using homo- and heteronuclear correlated spectroscopy.





trans-**3**

Figure 2.

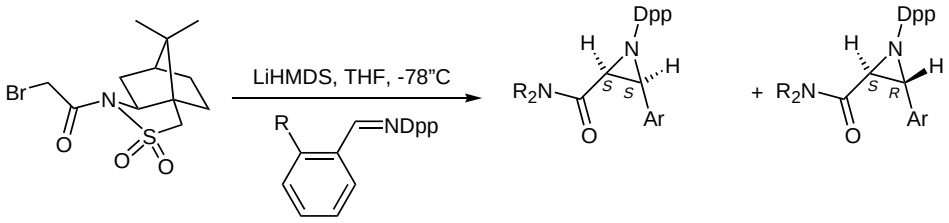
These data are completely at odds with a mechanism controlled by steric demand and may suggest that there are several mechanism at play, as discussed below.

2.3. Mechanism of ADZ Reaction[§]

General principles

Though there are many possible arrangements of reagents, the preferred rationalization for asymmetric aldol reactions

Table 1. Effect of imine substitution upon diastereoselectivity of ADZ reactions



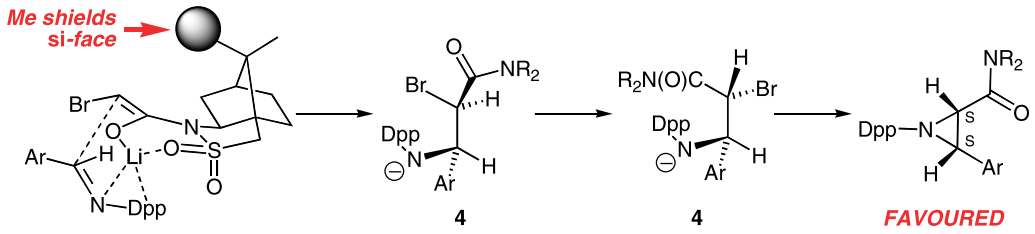
Entry	Ar	Yield (%)	cis:trans	^3J cis/trans (Hz)
1	Ph	71	100:0	6.2
2	2-NO_2–C_6H_4	72	100:0	5.8
3	2-F–C_6H_4	84	50:50	6.2/2.8
4	2-Cl–C_6H_4	68	20:80	6.1/2.8
5	2-Br–C_6H_4	67	0:100	2.6
6	2-I–C_6H_4	73	0:100	2.8
7	2-OMe–C_6H_4	65	0:100	3.1
8	2-Me–C_6H_4	87	50:50	6.0/2.8
9	2-Et–C_6H_4	93	63:37	6.1/2.8
10	2-CF_3–C_6H_4	69	0:100	2.7

the -imine derived from 2-nitrobenzaldehyde was *cis*-aziridine exclusively isolated. The latter observation might lead one to the conclusion that the polarity of the 2-substituent is unimportant in influencing the diastereoselectivity of the reaction and that the formation of *cis*-aziridine is due to the relatively small steric demands of the planar NO_2 substituent. This conclusion is endorsed by the results obtained from the ADZ reactions of the imines derived from *ortho*-halo benzaldehydes (Table 1, entries 3–6), which seem to indicate a clear connection between size and selectivity: 2-fluorobenzaldimine gives a 50:50 mixture of *cis*- and *trans*-aziridines, 2-chlorobenzaldimine a 20:80 ratio (as described above), while the 2-bromo- and 2-iodobenzaldimines furnish only *trans*-aziridines. In all the reactions of the halogenated substrates, the overall yields were similar to, or better than (in the case of the 2-fluoro and 2-iodo compounds) the reaction of the parent imine. The presence of a more powerfully π-donating electronegative substituent, a 2-methoxy group, had a similar effect upon the diastereoselectivity of the reaction, with only *trans*-aziridine obtained. However, when the ADZ reaction was carried out using 2-methylbenzaldimine, in which the substituent has a greater steric demand than any of the halogens, a 50:50 mixture of *cis*- and *trans*-aziridines was obtained, in excellent yield. Given the relative *A*-values (for instance, $A_{Br}=$ 2.01–2.80 kJ mol^{-1}, whereas $A_{Me}=7.28$ kJ mol^{-1}), this result does not tally with a reaction proceeding purely under the control of steric effects (vide infra). Furthermore, the 2-trifluoromethylphenyl imine gave only *trans*-aziridine (entry 9), whereas the ethyl substituted analogue reacted to give the cis-isomer as the dominant product (cis:trans = 1.7:1, entry 10).

mediated by lithium enolates of camphorsultam derivatives invokes a twisted boat-like transition state, in which there is a chelation between one of the S=O bonds and the apical lithium atom of the enolate.[3] Thus, in the (*Z*)-enolate produced by deprotonation of *N*-bromoacetyl-(2*S*)-camphorsultam, the *si*-face is powerfully shielded by the methyl group, which is *syn*- to the sultam unit, and these enolates inherently favour *re*-face interactions with incoming electrophiles.

Although likely to share the general features of aldol reactions, the ADZ reaction is complicated by several additional factors: firstly, the reaction is considerably slower than the aldol reaction. Secondly, there is an additional (and polar) substituent in the shape of the diphenylphosphinyl group. Finally, there is the question of imine stereochemistry: the barrier to imine inversion is variable, but such isomerizations are relatively facile under a range of conditions.[4] As in sultam aldol reactions, the enolate's *re*-face is, in all cases, more accessible: as the imine approaches the enolate, its substituent is placed *anti*- to the sultam sub-unit, leading to the transition state shown in Scheme 3 (note that in any of the chelated transition states there is an unavoidable interaction of the imine substituent and the α-bromo group-vide infra). In addition, it is likely that the Dpp group will coordinate to the lithium atom of the enolate, through the polar P=O bond,

[§] In our original description (McLaren, A. B.; Sweeney, J. B. *Org. Lett.*, **1999**, *1*, 1339) of the trans-selective ADZ reaction, the diagrammatic representaion of the transition states involved were reproduced incorrectly; we thank Professor D. Tanner for drawing our attention to this fact.



Scheme 3.

though this interaction may be weak (a full coordination would form a four-membered ring).

This preferred, *re–re*, interaction would lead to a 2′*S*,3′*S*-aziridine when using (2*S*)-sultam, via the corresponding 2′*R*, 3′*S*-bromoamide **4**: this hypothetical prediction is fulfilled in practice. However, although it is clear that the reaction proceeds via a *re–re* interaction, it is not a trivial matter to deduce the precise nature of the TS: we must consider three options.

Chair, boat or open TS?

As adumbrated above, the face selectivity of the ADZ reaction can be easily ascertained from the stereochemistry of the products (assuming *Z*-configuration in the enolate and *E*-configuration in the imine). It is less clear whether this stereochemical course of action arises from a closed or open transition state: it is even less obvious whether the closed TS would prefer a chair or boat arrangement.

Closed TS, chair or boat conformation

It is difficult to construct a convincing *re–re* Zimmerman–Traxler-like transition state (Scheme 4) for this ADZ reaction: there clearly is a unfavourable interaction between the imine CH and the methylene group adjacent to the C–N bond of the camphor sub-unit. As shown in the figure, this repulsive interaction is not greatly ameliorated by a change in conformation from chair→boat. The tetracyclic TS is configured in this manner when coordination to the lithium atom of the enolate occurs through the pseudoaxial rather than the pseudoequatorial S=O bond.

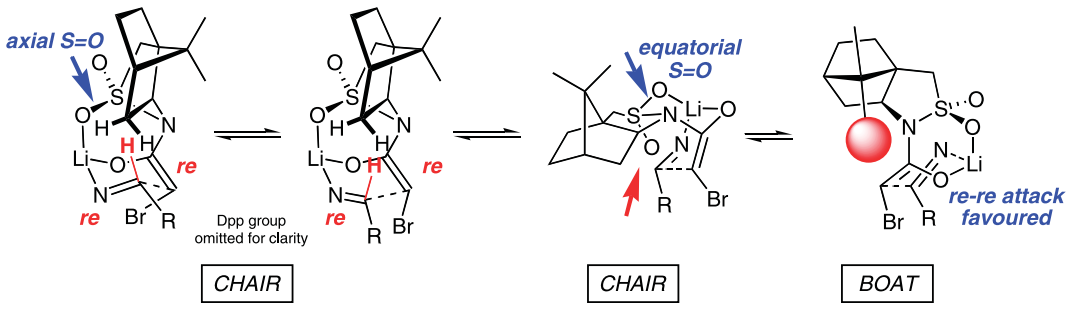
If the pseudoequatorial S=O bond is used in coordination, an alternative Zimmerman–Traxler TS is still accessible, but even more severe steric interactions are evident. Thus, it seems likely that a twisted boat TS is in operation. In this arrangement, one of the *gem*-dimethyl groups of the terpene bridge still provides a powerful shielding influence, the pseudoequatorial S=O–Li interaction is in place and the R substituent is *anti*-to the camphor ring. This is a *re–re* interaction, leading to the 2′*S*,3′*S*-configured aziridine products observed.

Inversion of diastereoselectivity

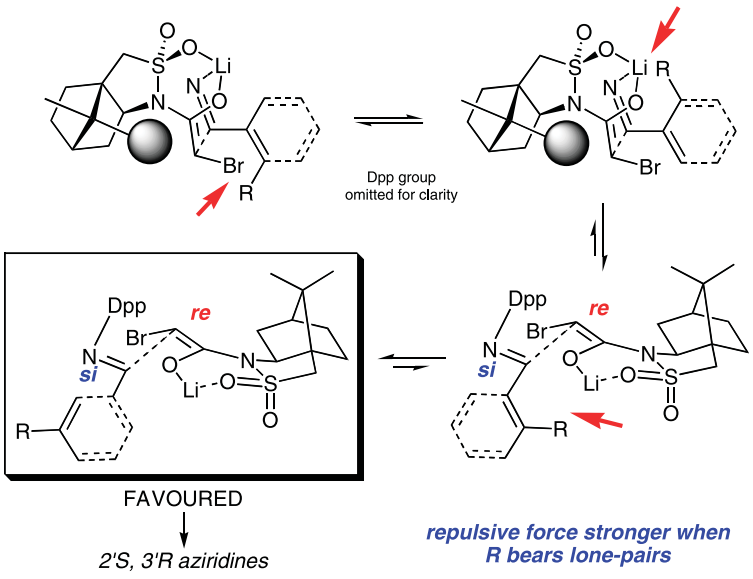
As described above, ADZ reaction of *ortho*-substituted imines can give 2′*S*,3′*R*-aziridines from 2*S*-bromoacyl camphorsultam and we must modify our mechanistic rationâle accordingly. Such products arise from a *re*-enolate–*si*-imine interaction, which cannot be easily accommodated within a closed transition state: the chelated nature of the enolate precludes a simple change in the direction of approach of the reagents. We suggest that an open transition state is in operation, as shown in Scheme 5; this open TS is favoured, we believe, due to the repulsive interaction between the imine γ-substituent (an *ortho*-substituent in the case of aryl imines and an allylic substituent in the case of an α,β-unsaturated imine) and the enolate bromine in a cyclic TS. Thus, there is an equilibrium between conformers in which the R substituent is either *syn*- or *anti*-to the enolate α-bromo substituent.

In both conformers, there are repulsive interactions, which can destabilize the arrangement though the major contributor is certainly the Br–R interaction (indicated by bold arrows on the Scheme). A switch to an open TS, though not without steric interactions, is certainly less compressed than the closed TS, and so a *re*-enolate-*si*-imine interaction is favoured, leading to 2′*S*,3′*R*-configured aziridines.

As alluded to above, the variation in selectivity is not controlled by purely steric demands: recall that the

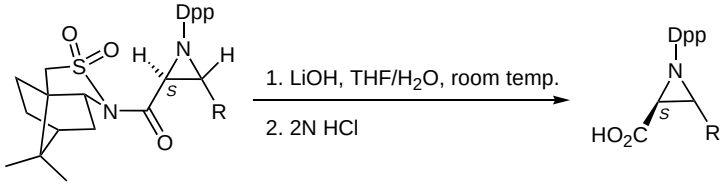


Scheme 4.



Scheme 5.

Table 2. Hydrolytic removal of auxiliary from *cis*- and *trans*-aziridines



Entry	R	Yield (%)
1	*trans*-$Me_2C{=}CH$	50
2	*trans*-2-Cl–C_6H_4	45
3	*trans*-2-F_3C–C_6H_4	57
4	*cis*-2-Me–C_6H_4	81
5	*cis*-2-Et–C_6H_4	65

reaction with R=Me is less selective than with R=OMe, despite the effective smaller size of the methoxy substituent (O vs CH_2). This suggests that there is a polar phenomenon also in play, perhaps due to the lone-pair/lone-pair repulsion, which would be present with oxygen or halogeno substituents, but not with alkyl ones. Such a phenomenon would also rationalize the observation that an *ortho*-CF_3 group causes a complete inversion in stereoselectivity, whereas the *ortho*-CH_3 group engenders a non-selective reaction (giving a 50:50 mixture of cis- and trans-isomers). It does not, however, explain why an *ortho*-ethyl group gives a mixture of aziridines dominated by the cis-form (cis:trans=63:37).

Cleavage of the auxiliary

We have also demonstrated that a representative cross-section of these *trans*-aziridines can be hydrolyzed to give the corresponding aziridine carboxylates, in a manner analogous to that described for the cis-compounds (Table 2). However, the yields of hydrolysis are lower than observed in the hydrolysis of analogous *cis*-aziridines, perhaps reflecting a more hindered trajectory for the incoming nucleophile.

3. Conclusion

We have developed a practical ADZ reaction, which allows the preparation of chiral aziridine derivatives in good yield. Depending on the substitution pattern of the imine, the inherent cis-selectivity of the process can be inverted to give exclusively trans-configured products. We are currently attempting to expand further the scope of this process, and studying the underlying factors responsible for the stereoselectivity observed.

4. Experimental

4.1. General techniques

All organic solvents were distilled prior to use and all reagents were purified by standard procedures.[5] 'Petrol' refers to the fraction of petroleum ether with the boiling range 40–60 °C and 'ether' refers to diethyl ether. Ether and THF were distilled from sodium benzophenone ketyl; toluene from sodium; dichloromethane, triethylamine, acetonitrile from calcium hydride, methanol from magnesium methoxide and diisopropylethylamine from potassium

hydroxide. Imines were prepared according to literature methods.[6] Other chemicals were purchased from Aldrich Chemical Co. or prepared by literature methods.

Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected. Spectra were recorded on Perkin Elmer 881 or Paragon 1000 spectrophotometers. Optical rotations were measured using a Perkin Elmer 241 MC polarimeter and are quoted in 10^{-1} deg cm^2 g^{-1}. Mass spectra were recorded on VG9090 or Fisons Autospec mass spectrometers. ^{1}H and ^{13}C NMR spectra were recorded on Jeol GX-270, Jeol GX-400, Lambda 300, Bruker DPX-250 or Bruker AX-400 spectrometers. Unless otherwise stated, deuterochloroform was used as solvent and tetramethylsilane was the internal standard. Chemical shifts in ^{1}H NMR spectra are expressed as ppm downfield from tetramethylsilane, and in ^{13}C NMR, relative to the internal solvent standard. Coupling constants (*J*) are quoted in Hz.

Reactions involving chemicals or intermediates sensitive to air or moisture were conducted under a nitrogen or argon atmosphere in oven- or flame-dried apparatus. Flash chromatography was performed using Merck Kieselgel 60 or Fluka Kieselgel 60 silica gel. Analytical thin-layer chromatography was performed using either precoated Merck Kieselgel 60 F_{254} glass-backed plates, or precoated Merck Kieselgel 60 F_{254} aluminium backed plates and were visualised under UV at 254 nm and by staining with iodine and/or an acidic ammonium molybdate dip.

X-ray data obtained from *trans*-**3** has been deposited at CCDC (reference number CCDC 291092).

^{13}C NMR spectra of *N*-Dpp compounds are complicated by rotameric isomers, which often leads to the appearance of 'excess' resonances in the aromatic region of the spectra; the situation is further complicated by the difficulty in obtaining precise coupling constants. Rather than refer to the entire region of the spectra as being a 'multiplet', the data quoted describes the actual appearance of the spectra.

4.2. General procedure for aza-Darzens reaction: synthesis of *cis*- and *trans*-2,3 substituted aziridines

(2*R*)-(−)-(*N*-Bromoacetyl)bornane-10,2-sultam, (1.0 equiv), was dissolved in THF (25 mL) and cooled to −78 °C. LiHMDS in THF (1.1 equiv) was then added dropwise, and the resulting pale yellow solution stirred for 30 min. Phosphinylimine (typically 1.0 equiv) was then added at −78 °C as a solution in THF (10 mL). The reaction mixture was then stirred for over 2 h at −78 °C, after which time the reaction was judged to have reached completion by TLC and the mixture was quenched with saturated ammonium chloride solution (20 mL). The aqueous layer was extracted with EtOAc (20 mL, 2×10 mL), the organic layers were then combined, washed with brine, dried ($MgSO_4$), filtered, and the solvent removed in vacuo, to afford the crude aziridine.

4.2.1. *cis*-2*S*,2′*S*,3′*S*-*N*-[(1-Diphenylphosphinyl-3-(2-methylpropenyl)-2-aziridinyl)carbonyl]bornane-10, 2-sultam (*cis*-1b).

Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10, 2-sultam (336 mg, 1.0 mmol), LiHMDS in THF (1.1 mL, 1.0 M, 1.1 mmol) and *P*,*P*-diphenyl-*N*-(2-methylpropenylmethylene)phosphinic amide (283 mg, 1.0 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford **1b**, as a colourless solid (214 mg, 40%); R_f 0.55 (EtOAc); $[\alpha]_D^{20}$ +74.1 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 3058, 2966, 1698, 1440, 1338, 1168, 1268, 1127, 735, 705 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.85 (3H, s), 0.93 (3H, s), 1.13–1.26, 1.76–1.81 and 1.95–2.01 (7H, m), 1.28 (3H, s), 1.53 (3H, s), 3.29 and 3.38 (2H, 2×d, *J*=13.9 Hz), 3.45–3.51 (1H, m), 3.73–3.91 (2H, m), 5.32 (1H, d, *J*=9.2 Hz), 7.29–7.41 (6H, m), 7.76–7.81 and 7.92–7.97 (4H, m); δ_C (100 MHz, $CDCl_3$) 17.5, 25.5, 19.7, 20.6, 26.2, 32.6, 38.2, 40.0, 44.4, 44.5, 47.7, 49.0, 52.6, 64.8, 118.6, 127.9, 128.0, 128.2, 128.4, 128.5, 128.5, 131.2, 131.4, 131.5, 131.6, 131.8, 131.9, 132.1, 132.2, 132.7, 133.0, 134.1, 142.0, 166.7; MS (CI) *m*/*z* 538 ([M]$^+$, 11%), 417 (9), 296 (62), 219 (29), 201 (100), 77 (18); HRMS found: [M]$^+$538.2099 $C_{29}H_{36}N_2O_4PS$ requires 538.2055.

4.2.2. 2*S*-*N*-[1′-Diphenylphosphinyl-4′,4′-dimethyl-2′,3′-dihydro-1*H*-pyrrole-5′-carbonyl]bornane-10, 2-sultam (2).

Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10, 2-sultam (336 mg, 1.0 mmol), LiHMDS in THF (1.1 mL, 1.0 M, 1.1 mmol) and *P*,*P*-diphenyl-*N*-(2-methylpropenylmethylene)phosphinic amide (283 mg, 1.0 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford **2** as a colourless solid (109 mg, 20%); R_f 0.36 (EtOAc); $[\alpha]_D^{20}$ +66.4 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 3056, 2968, 1687, 1440, 1342, 1168, 1267, 1125, 741, 705 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.85 (3H, s), 0.94 (3H, s), 1.23 (3H, s), 1.51 (3H, s), 1.01–1.36 and 1.80–2.11 (7H, 2×m), 3.39 and 3.41 (2H, 2×d, *J*=13.2 Hz), 3.85 (1H, m), 4.17 (1H, m), 4.80 (1H, m), 4.99 (1H, m), 7.36–7.41 (6H, m), 7.82–7.90 (4H, m); δ_C (100 MHz, $CDCl_3$) 18.1, 25.5, 19.7, 20.6, 26.3, 32.8, 38.0, 44.6, 47.7, 48.5, 52.8, 53.3, 56.5, 65.5, 122.3, 128.1, 128.2, 128.3, 128.3, 128.4, 128.6, 131.2, 131.4, 131.5, 131.7, 131.8, 131.9, 132.0, 132.1, 132.2, 132.3, 132.4, 132.4, 133.6, 137.9, 167.2; MS (CI) *m*/*z* 539 ([M]$^+$, 13%), 475 (6), 419 (16), 324 (20), 284 (100), 218 (68), 152 (34); HRMS found: [M]$^+$539.2127, $C_{29}H_{35}N_2O_4PS$ requires 539.2133.

4.2.3. *cis*-2*S*,2′*S*,3′*S*-*N*-[(1-Diphenylphosphinyl-3-(2-fluorophenyl)-2-aziridinyl)carbonyl]bornane-10, 2-sultam (Table 1, entry 3).

Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10, 2-sultam (336 mg, 1.0 mmol), LiHMDS in THF (1.1 mL, 1.0 M, 1.1 mmol) and *P*,*P*-diphenyl-*N*-(2-fluorophenylmethylene)phosphinic amide (323 mg, 1.0 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (243 mg, 42%); R_f 0.50 (petrol/EtOAc 1:3); $[\alpha]_D^{20}$ +16.6 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 3057, 2964, 1703, 1441, 1340, 1176, 1271, 1129, 758, 733, 704 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.89, (3H, s), 0.93 (3H, s), 1.19–1.28 and 1.80–1.99 (7H, 2×m), 3.27 and 3.38 (2H, 2×d, *J*=13.6 Hz), 3.64 (1H, m), 4.18 and 4.48 (2H, 2×dd,

J_P=15.8 Hz, J=6.2 Hz), 6.94–7.59 (10H, m), 7.92–8.15 (4H, m); δ_C (100 MHz, $CDCl_3$) 19.7, 20.6, 26.3, 32.5, 38.0, 38.5, 41.4, 44.6, 47.7, 49.0, 52.4, 64.5, 114.7, 123.4, 128.4, 128.6, 128.7, 129.1, 129.6, 129.7, 130.8, 130.9, 131.5, 131.6, 131.7, 131.8, 132.0, 132.2, 160.8, 163.4; MS (CI) *m/z* 579 ($[MH]^+$, 96%), 515 (42), 419 (40), 379 (27), 297 (28), 218 (100), 135 (30); HRMS found: $[MH]^+$579.1874, $C_{31}H_{33}FN_2O_4PS$ requires 579.1883.

4.2.4. *trans*-2*S*,2′*S*,3′*R*-*N*-[(1-Diphenylphosphinyl-3-(2-fluorophenyl)-2-aziridinyl)carbonyl]bornane-10, 2-sultam (Table 1, entry 3). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10, 2-sultam (336 mg, 1.0 mmol), LiHMDS in THF (1.1 mL, 1.0 M, 1.1 mmol) and *P*,*P*-diphenyl-*N*-(2-fluorophenylmethylene)phosphinic amide (323 mg, 1.0 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (243 mg, 42%); R_f 0.45 (petrol/EtOAc 1:3); $[\alpha]_D^{20}$ +83.5 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 3057, 2964, 1687, 1440, 1339, 1169, 1287, 1139, 742, 700 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.83 (3H, s), 0.87 (3H, s), 1.16–1.36 and 1.70–1.97 (7H, 2×m), 3.03 and 3.36 (2H, 2×d, J= 13.9 Hz), 3.78 (1H, m), 4.20 and 4.33 (2H, 2×dd, J_P= 13.4 Hz, J=2.8 Hz), 6.71–7.90 (14H, m); δ_C (100 MHz, $CDCl_3$) 20.1, 21.0, 26.7, 33.0, 38.2, 40.8, 41.2, 44.8, 48.0, 49.2, 53.1, 65.5, 115.1, 124.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 129.1, 130.4, 130.4, 131.7, 131.8, 131.9, 132.0, 132.4, 132.5, 163.9, 165.6; MS (CI) *m/z* 579 ($[MH]^+$, 100%), 515 (71), 419 (67), 379 (41), 297 (35), 201 (78); HRMS found: $[MH]^+$579.1902, $C_{31}H_{33}FN_2O_4PS$ requires 579.1883.

4.2.5. *cis*-2*S*,2′*S*,3′*S*-*N*-[(1-Diphenylphosphinyl-3-(2-chlorophenyl)-2-aziridinyl)carbonyl]bornane-10, 2-sultam (Table 1, entry 4). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10, 2-sultam (336 mg, 1.0 mmol), LiHMDS in THF (1.1 mL, 1.0 M, 1.1 mmol) and *P*,*P*-diphenyl-*N*-(2-chlorophenylmethylene)phosphinic amide (340 mg, 1.0 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (81 mg, 13%); R_f 0.63 (EtOAc); $[\alpha]_D^{20}$ +28.7 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 3057, 2964, 1703, 1440, 1341, 1128, 1266, 1169, 745, 705, 644 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.78–0.83 (6H, m), 1.12–1.20 and 1.72–1.97 (7H, 2×m), 3.22 and 3.30 (2H, 2×d, J=13.9 Hz), 3.57–3.60 (1H, m), 4.11–4.50 (2H, 2×dd, J_P=15.9 Hz, J= 6.1 Hz), 7.10–7.57 and 7.85–8.03 (14H, 2×m); δ_C (100 MHz, $CDCl_3$) 19.7, 20.6, 26.3, 32.5, 38.1, 40.7, 42.3, 44.6, 47.7, 49.0, 52.5, 64.6, 126.0, 128.4, 128.6, 128.7, 129.1, 129.2, 129.6, 130.6, 130.8, 131.6, 131.7, 131.7, 131.8, 131.8, 131.9, 132.1, 132.3, 134.6, 163.7; MS (CI) *m/z* 595 ($[MH]^+$, 66%), 531 (60), 419 (100), 313 (43), 201 (91), 77 (32); HRMS found: $[MH]^+$595.1594, $C_{31}H_{34}N_2O_4PS$ requires 595.1588.

4.2.6. *trans*-2*S*,2′*S*,3′*R*-*N*-[(1-Diphenylphosphinyl-3-(2-chlorophenyl)-2-aziridinyl)carbonyl]bornane-10, 2-sultam (Table 1, entry 4). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10, 2-sultam (336 mg, 1.0 mmol), LiHMDS in THF (1.1 mL, 1.0 M, 1.1 mmol) and *P*,*P*-diphenyl-*N*-(2-chlorophenylmethylene)phosphinic amide (340 mg, 1.0 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (325 mg, 55%); R_f 0.56 (EtOAc); $[\alpha]_D^{20}$ +59.4 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 3056, 2985, 1705, 1440, 1338, 1168, 1266, 1126, 738, 706, 623 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.75 (3H, s), 0.80 (3H, s), 1.01–1.29 and 1.65–1.89 (7H, 2×m), 3.23 and 3.28 (2H, 2×d, J= 13.6 Hz), 3.72 (1H, m), 4.16 and 4.30 (2H, 2×dd, J_P= 13.3 Hz, J=2.8 Hz), 7.03–7.10 and 7.19–7.34 (10H, 2×m), 7.63–7.67 and 7.79–7.83 (4H, 2×m); δ_C (100 MHz, $CDCl_3$) 19.7, 20.6, 26.3, 32.5, 37.8, 41.3, 44.0, 44.4, 47.6, 48.8, 52.7, 65.1, 126.5, 128.0, 128.1, 128.1, 128.3, 128.4, 128.9, 129.4, 131.2, 131.6, 131.7, 132.5, 133.0, 134.3, 135.5, 164.9; MS (CI) *m/z* 594 ($[M]^+$, 19%), 559 (49), 219 (68), 201 (100), 77 (27); HRMS found: $[M]^+$594.1559, $C_{31}H_{34}N_2O_4PS$ requires 594.1509.

4.2.7. *trans*-2*S*,2′*S*,3′*R*-*N*-[(1-Diphenylphosphinyl-3-(2-bromophenyl)-2-aziridinyl)carbonyl]bornane-10, 2-sultam (Table 1, entry 5). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10, 2-sultam (336 mg, 1.0 mmol), LiHMDS in THF (1.1 mL, 1.0 M, 1.1 mmol) and *P*,*P*-diphenyl-*N*-(2-bromophenylmethylene)phosphinic amide (386 mg, 1.0 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (428 mg, 67%); R_f 0.53 (EtOAc); $[\alpha]_D^{20}$ +13.5 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 3056, 2966, 1705, 1441, 1336, 1188, 1267, 1128, 740, 705 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.88 (3H, s), 0.89 (3H, s), 1.21–1.38 and 1.80–2.02 (7H, 2×m), 3.37 and 3.42 (2H, 2×d, J= 13.9 Hz), 3.86 (1H, m), 4.24 and 4.43 (2H, 2×dd, J_P= 13.2 Hz, J=2.6 Hz), 7.10–7.14, 7.24–7.28 and 7.35–7.45 (10H, m), 7.78–7.83 and 7.92–7.97 (4H, m); δ_C (100 MHz, $CDCl_3$) 9.8, 20.6, 26.4, 32.7, 37.9, 41.9, 46.1, 44.5, 47.7, 48.8, 52.8, 65.7, 125.4, 127.2, 127.6, 128.1, 128.2, 128.4, 128.4, 128.6, 128.7, 129.5, 129.7, 129.9, 131.3, 131.5, 131.6, 131.7, 131.8, 131.9, 132.4, 132.5, 133.0, 133.3, 133.3, 133.7, 134.4, 134.5, 164.8; MS (CI) *m/z* 639 ($[MH]^+$, 32%), 573 (30), 419 (50), 357 (11), 219 (100), 135 (23); HRMS found: $[MH]^+$639.1089, $C_{31}H_{33}BrN_2O_4PS$ requires 639.1082.

4.2.8. *trans*-2*S*,2′*S*,3′*R*-*N*-[(1-Diphenylphosphinyl-3-(2-iodophenyl)-2-aziridinyl)carbonyl]bornane-10, 2-sultam (Table 1, entry 6). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10, 2-sultam (202 mg, 0.6 mmol), LiHMDS in THF (0.66 mL, 1.0 M, 0.66 mmol) and *P*,*P*-diphenyl-*N*-(2-iodophenylmethylene)-phosphinic amide (259 mg, 0.6 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (300 mg, 73%); R_f 0.51 (EtOAc); $[\alpha]_D^{20}$ +73.5 (*c* 1, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.77 (3H, s), 0.79 (3H, s), 1.07–1.35, 1.70–1.97 (7H, 2×m), 3.03 and 3.37 (2H, m), 3.78 (1H, m), 4.10 and 4.26 (2H, 2×dd, J_P=13.1 Hz, J=2.8 Hz), 6.86 (1H, m), 7.19–7.35 (8H, m), 7.58–7.87 (5H, m); δ_C

(60 MHz, $CDCl_3$) 20.2, 21.2, 26.9, 33.1, 38.3, 43.1, 50.8, 44.9, 48.1, 49.3, 53.3, 65.7, 100.6, 128.5, 128.5, 128.6, 128.7, 128.8, 128.9, 130.4, 131.3, 132.0, 132.2, 132.3, 132.4, 133.0, 133.3, 135.1, 136.9, 136.9, 139.5, 165.0; MS (CI) *m/z* 687 ($[MH]^+$, 10%), 234 (33), 216 (100), 152 (29); HRMS found: $[MH]^+$687.0969, $C_{31}H_{33}IN_2O_4PS$ requires 687.0943.

4.2.9. *trans*-2*S*,2′*S*,3′*S*-*N*-[(1-Diphenylphosphinyl-3-(2-methoxyphenyl)-2-aziridinyl)carbonyl]bornane-10,2-sultam (Table 1, entry 7). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10,2-sultam (202 mg, 0.6 mmol), LiHMDS in THF (0.7 mL, 1.0 M, 0.7 mmol) and *P*,*P*-diphenyl-*N*-(2-methoxyphenylmethylene)phosphinic amide (200 mg, 0.6 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (227 mg, 65%); R_f 0.37 (EtOAc); $[\alpha]_D^{20}$ +86.4 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 3057, 2965, 1686, 1441, 1343, 1172, 1267, 1124, 735, 702 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.82 (3H, s), 0.83 (3H, s), 1.16–1.29 and 1.72–1.96 (7H, 2×m), 3.23 (3H, s), 3.29 and 3.36 (2H, 2×d, *J*=13.7 Hz), 3.77–3.78 (1H, m), 4.24–4.31 (2H, m), 6.52 (1H, m), 6.81–6.85 (1H, m), 7.12–7.36 (8H, m), 7.69–7.74 and 7.83–7.88 (4H, m); δ_C (100 MHz, $CDCl_3$) 19.7, 20.7, 26.3, 32.6, 38.0, 39.6, 43.4, 44.5, 47.7, 48.8, 52.8, 54.4, 65.1, 109.5, 120.1, 121.8, 121.8, 127.8, 127.9, 128.0, 128.2, 128.3, 129.6, 131.1, 131.3, 131.4, 131.6, 131.6, 131.7, 131.7, 132.0, 133.3, 133.6, 134.9, 158.9, 166.1; MS (CI) *m/z* 591 ($[MH]^+$, 9%), 391 (100), 350 (24), 201 (66), 148 (75), 77 (39); HRMS found: $[MH]^+$591.2072, $C_{32}H_{36}N_2O_5PS$ requires 591.2083.

4.2.10. *cis*-2*S*,2′*S*,3′*S*-*N*-[(1-Diphenylphosphinyl-3-(2-methylphenyl)-2-aziridinyl)carbonyl]bornane-10,2-sultam (Table 1, entry 8). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10,2-sultam (270 mg, 0.8 mmol), LiHMDS in THF (0.9 mL, 1.0 M, 0.9 mmol) and *P*,*P*-diphenyl-*N*-(2-methylphenylmethylene)phosphinic amide (255 mg, 0.8 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (200 mg, 43%); R_f 0.63 (EtOAc); $[\alpha]_D^{20}$ +34.8 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 3059, 2964, 1704, 1440, 1337, 1167, 1268, 1128, 770, 737, 705 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.98 (6H, 2s), 1.30–1.38, 1.87–1.90 and 1.98–2.09 (7H, m), 2.53 (3H, s), 3.37 and 3.49 (2H, 2×d, *J*=13.7 Hz), 3.70–3.73 (1H, m), 4.35 and 4.49 (2H, 2×dd, J_P=11.7 Hz, *J*=6.0 Hz), 7.16–7.28 (3H, m), 7.49–7.63 and 7.73–7.75 (7H, 2×m), 8.10–8.21 (4H, m); δ_C (100 MHz, $CDCl_3$) 19.6, 20.2, 21.0, 26.7, 32.9, 38.4, 40.9, 43.6, 44.9, 48.2, 49.3, 53.1, 65.2, 125.4, 128.2, 128.3, 128.8, 128.9, 129.1, 129.1, 130.1, 130.7, 130.9, 131.0, 131.2, 132.1, 132.2, 132.7, 133.2, 138.3, 164.3; MS (CI) *m/z* 575 ($[MH]^+$, 100%), 510 (12), 375 (24), 201 (59), 131 (25), 77 (16); HRMS found: $[MH]^+$575.2101, $C_{32}H_{36}N_2O_4PS$ requires 575.2134.

4.2.11. *trans*-2*S*,2′*S*,3′*R*-*N*-[(1-Diphenylphosphinyl-3-(2-methylphenyl)-2-aziridinyl)carbonyl]bornane-10,2-sultam (Table 1, entry 8). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10,2-sultam (270 mg, 0.8 mmol), LiHMDS in THF (0.9 mL, 1.0 M, 0.9 mmol) and *P*,*P*-diphenyl-*N*-(2-methylphenylmethylene)phosphinic amide (255 mg, 0.8 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (200 mg, 43%); R_f 0.49 (EtOAc); $[\alpha]_D^{20}$ +53.0 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 3057, 2965, 1698, 1440, 1337, 1168, 1267, 1125, 740, 707 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.56 (3H, s) 0.59 (3H, s), 0.91–1.07 and 1.48–1.79 (7H, 2×m), 3.06 and 3.11 (2H, 2×d, *J*=14.3 Hz), 3.54 (1H, m), 3.87 and 3.97 (2H, 2×dd, J_P=11.9 Hz, *J*=2.8 Hz), 6.70–7.17 (10H, m), 7.50–7.66 (4H, m); δ_C (100 MHz, $CDCl_3$) 18.7, 19.7, 20.7, 26.3, 32.5, 37.7, 42.2, 44.0, 44.4, 47.6, 48.7, 52.8, 65.2, 125.7, 126.3, 127.9, 128.0, 128.1, 128.2, 128.2, 128.4, 129.7, 131.5, 131.6, 131.6, 131.7, 131.9, 132.1, 132.2, 136.4, 137.9, 165.3; MS (CI) *m/z* 575 ($[MH]^+$, 28%), 511 (25), 419 (37), 219 (100), 131 (16), 77 (19); HRMS found: $[MH]^+$575.2109, $C_{32}H_{36}N_2O_4PS$ requires 575.2134.

4.2.12. *cis*-2*S*,2′*S*,3′*R*-*N*-[(1-Diphenylphosphinyl-3-(2-ethylphenyl)-2-aziridinyl)carbonyl]bornane-10,2-sultam (Table 1, entry 9). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10,2-sultam (672 mg, 2.0 mmol), LiHMDS in THF (2.1 mL, 1.0 M, 2.1 mmol) and *P*,*P*-diphenyl-*N*-(2-ethylphenylmethylene)phosphinic amide (667 mg, 2.0 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (700 mg, 59%); R_f 0.51 (petrol/EtOAc 1:3); $[\alpha]_D^{20}$ +40.0 (*c* 1, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 0.79 (6H, m), 1.07 (3H, t, *J*=7.6 Hz), 1.04–1.20 and 1.68–1.86 (7H, 2×m), 2.53–2.68 and 2.74–2.89 (2H, 2×dt, *J*=15.1, 7.6 Hz), 3.17 and 3.29 (2H, 2×d, *J*=13.8 Hz), 3.52 (1H, m), 4.15 and 4.31 (2H, 2×dd, J_P=15.9 Hz, *J*=6.1 Hz), 7.05–7.09 (3H, m), 7.29–7.40 (H, m), 7.88–8.00 (4H, m); δ_C (60 MHz, $CDCl_3$) 15.0, 20.2, 21.0, 25.3, 26.7, 32.9, 38.4, 41.2, 43.2, 44.9, 48.1, 49.2, 53.0, 65.2, 125.4, 127.9, 128.3, 128.5, 128.8, 128.4, 129.0, 129.1, 130.3, 130.4, 132.0, 132.1, 132.2, 132.2, 132.6, 132.6, 132.7, 144.0, 164.4; MS (CI) *m/z* 589 ($[MH]^+$, 100%), 419 (10), 389 (17), 216 (27), 134 (14), 66 (11); HRMS found: $[MH]^+$589.2295, $C_{33}H_{38}N_2O_4PS$ requires 589.2290.

4.2.13. *trans*-2*S*,2′*S*,3′*R*-*N*-[(1-Diphenylphosphinyl-3-(2-ethylphenyl)-2-aziridinyl)carbonyl]bornane-10,2-sultam (Table 1, entry 9). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10,2-sultam (672 mg, 2.0 mmol), LiHMDS in THF (2.1 mL, 1.0 M, 2.1 mmol) and *P*,*P*-diphenyl-*N*-(2-ethylphenylmethylene)phosphinic amide (667 mg, 2.0 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (400 mg, 34%); R_f 0.29 (EtOAc); $[\alpha]_D^{20}$ +63.5 (*c* 1, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 0.77 (3H, s), 0.80 (3H, s), 0.95 (3H, t, *J*=7.5 Hz), 1.15–1.27 and 1.71–1.90 (7H, 2×m), 3.27 and 3.33 (2H, 2×d, *J*=13.8 Hz), 3.77 (1H, m), 4.05 and 4.26 (2H, 2×dd, J_P=13.3 Hz, *J*=2.8 Hz), 6.99–7.37 (10H, m), 7.78–7.80 (4H, m); δ_C (60 MHz, $CDCl_3$) 15.1, 20.2, 21.2, 25.6, 26.9, 33.1, 38.2,

43.3, 43.7, 44.9, 48.2, 49.2, 53.3, 65.7, 126.3, 126.5, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8, 129.0, 131.7, 132.0, 132.1, 132.2, 132.3, 132.6, 133.2, 133.8, 135.3, 144.2, 165.6; MS (CI) *m/z* 589 ([MH]+, 100%), 387 (17), 334 (10), 201 (39), 135 (11); HRMS found: $[MH]^+$589.2275, $C_{33}H_{38}N_2O_4PS$ requires 589.2290.

4.2.14. *trans*-2*S*,2′*S*,3′*R*-*N*-[(1-Diphenylphosphinyl-3-(2-trifluoromethylphenyl)-2-aziridinyl)carbonyl]bornane-10, 2-sultam (Table 1, entry 10). Following the general procedure described above *N*-bromoacetyl-2*S*-bornane-10, 2-sultam (672 mg, 2.0 mmol), LiHMDS in THF (2.1 mL, 1.0 M, 2.1 mmol) and *P*,*P*-diphenyl-*N*-(2-trifluoromethylphenylmethylene)phosphinic amide (747 mg, 2.0 mmol) were reacted to produce the crude aziridine. The resulting colourless solid was purified by flash chromatography eluting with petrol–EtOAc (1/9) to afford the product, as a colourless solid (860 mg, 69%); R_f 0.50 (EtOAc); $[\alpha]_D^{20}$ +52.6 (*c* 1, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 0.74 (3H, s), 0.80 (3H, s), 1.09–1.33 and 1.72–1.97 (7H, 2×m), 3.31 (2H, m), 3.79 (1H, m), 4.02 and 4.48 (2H, 2×dd, J_P=13.0 Hz, J=2.7 Hz), 7.29–7.46 (10H, m), 7.79–7.87 (4H, m); δ_C (60 MHz, $CDCl_3$) 20.2, 21.2, 26.9, 33.1, 38.1, 41.8, 44.8, 44.9, 48.2, 49.2, 53.3, 65.8, 126.1, 126.2, 127.9, 128.6, 128.7, 128.8, 128.9, 129.9, 130.4, 131.3, 132.0, 132.1, 132.2, 132.3, 132.3, 132.8, 133.3, 134.9, 164.3; MS (CI) *m/z* 629 ($[MH]^+$, 35%), 565 (25), 419 (78), 347 (20), 219 (100), 185 (32), 77 (10); HRMS found: $[MH]^+$629.1843, $C_{32}H_{33}N_2O_4PSF_3$ requires 629.1851.

4.3. General procedure for hydrolytic cleavage of camphorsultam auxiliary

2,3-Disubstituted *N*-diphenylphosphinyl aziridines bearing the camphor sultam moiety (typically 0.2 mmol), were dissolved in a THF–water (4/1) mixture (5 mL). Lithium hydroxide monohydrate (0.4 mmol) was then added and the resulting suspension stirred vigorously overnight. The excess solvent was removed under reduced pressure and the aqueous layer basified to pH 10 with saturated $NaHCO_3$ solution, and extracted with $CHCl_3$ (3×30 mL). The combined organic layers were washed with saturated $NaHCO_3$ solution (10 mL), dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to afford the 2*S*-bornane-10, 2-sultam. The aqueous layer was then combined with the base washings and acidified to pH 2 with saturated citric acid solution, and extracted with $CHCl_3$ (3×50 mL). The organic layers were combined, dried ($MgSO_4$), filtered and the solvent removed under reduced pressure to afford the *N*-diphenylphosphinyl-2-substituted-3-carboxyaziridines.

4.3.1. *trans*-2-Carboxy-*N*-diphenylphosphinyl-3-(2-methylpropenyl)aziridine (Table 2, entry 1). Following the general procedure described above *cis*-2*S*,2′*S*,3′*S*-*N*-[(1-diphenylphosphinyl-3-(2-methylpropenyl)-2-aziridinyl)-carbonyl]bornane-10, 2-sultam (108 mg, 0.2 mmol) afforded the product as a colourless oil (33 mg, 50%). $[\alpha]_D^{20}$ +17.8 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 1718, 1440, 1127, 1028, 757, 728, 697 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.26 (6H, 2s), 4.26 (1H, dd, J_P=13.4 Hz, J=5.8 Hz), 5.83 (1H, ddd, J=13.4, 13.4, 5.8 Hz), 5.93 (1H, d, J=13.4 Hz), 7.46–7.95 (10H, m); δ_C (60 MHz, $CDCl_3$) 30.0, 30.2, 57.0, 71.4, 125.1, 129.8, 130.1, 130.2, 130.3, 130.4, 132.2, 132.4, 132.6, 132.8, 133.5, 133.6, 133.8, 134.0, 134.3, 134.6, 142.7, 175.1; MS (CI) *m/z* 342 ($[MH]^+$, 15%), 314 (8), 297 (24), 219 (100), 130 (7), 84 (64), 66 (24); HRMS found: $[MH]^+$342.1273, $C_{19}H_{21}NO_3P$ requires 342.1259.

4.3.2. *trans*-2-Carboxy-*N*-diphenylphosphinyl-3-(2-chlorophenyl)aziridine (Table 2, entry 2). Following the general procedure described above *cis*-2*S*,2′*S*,3′*S*-*N*-[(1-diphenylphosphinyl-3-(2-chlorophenyl)-2-aziridinyl)carbonyl]bornane-10, 2-sultam (119 mg, 0.2 mmol) afforded the product as a colourless oil (34 mg, 45%). $[\alpha]_D^{20}$ +13.6 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 1733, 1439, 1130, 755, 729, 697 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 3.52 and 4.29 (2H, 2×dd, J_P=13.6 Hz, J=3.0 Hz), 7.12–7.80 (14H, m); MS (CI) *m/z* 354 ($[MH-CO_2]^+$, 35%), 318 (6), 219 (100), 154 (5), 130 (8), 77 (9); HRMS found: $[MH-CO_2]^+$354.0805, $C_{20}H_{18}ClNOP$ requires 354.0815.

4.3.3. *trans*-2-Carboxy-*N*-diphenylphosphinyl-3-(2-trifluoromethylphenyl)aziridine (Table 2, entry 3). Following the general procedure described above *cis*-2*S*,2′*S*,3′*S*-*N*-[(1-diphenylphosphinyl-3-(2-trifluoromethylphenyl)-2-aziridinyl)carbonyl]bornane-10, 2-sultam (126 mg, 0.2 mmol) afforded the product as a colourless oil (49 mg, 57%). $[\alpha]_D^{20}$ +15.4 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 1723, 1440, 1129, 1036, 757, 730, 695 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 3.43 and 4.48 (2H, 2×dd, J_P=12.7 Hz, J=2.7 Hz), 7.45–8.00 (14H, m); δ_C (60 MHz, $CDCl_3$) 42.5, 47.3, 123.9, 127.3, 127.3, 128.8, 130.1, 130.2, 130.2, 130.3, 130.4, 130.5, 132.8, 133.0, 133.1, 133.1, 133.2, 133.8, 133.9, 134.0, 169.9; MS (CI) *m/z* 432 ($[MH]^+$, 35%), 388 (21), 235 (100), 201 (11); HRMS found: $[MH]^+$432.0984, $C_{22}H_{18}NO_3PF_3$ requires 432.0976.

4.3.4. *cis*-2-Carboxy-*N*-diphenylphosphinyl-3-(2-methylphenyl)aziridine (Table 2, entry 4). Following the general procedure described above *cis*-2*S*,2′*S*,3′*S*-*N*-[(1-diphenylphosphinyl-3-(2-methylphenyl)-2-aziridinyl)carbonyl]-bornane-10, 2-sultam (115 mg, 0.2 mmol) afforded the product as a colourless oil (61 mg, 81%). $[\alpha]_D^{20}$ +2.6 (*c* 1, MeOH); IR ν_{max} (CCl_4) 1729, 1439, 1128, 1041, 755, 694 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.16 (3H, s), 3.47 and 3.94 (2H, 2×dd, J_P=15.7 Hz, J=6.6 Hz), 6.88–7.95 (14H, m); δ_C (60 MHz, $CDCl_3$) 19.3, 41.8, 42.1, 126.8, 128.9, 129.5, 130.3, 130.4, 130.5, 130.6, 131.1, 132.6, 132.8, 133.0, 133.1, 133.3, 133.5, 134.4, 134.4, 134.5, 138.4, 169.6; MS (CI) *m/z* 378 ($[MH]^+$, 35%), 334 (100), 235 (9), 201 (19), 134 (17); HRMS found: $[MH]^+$378.1248, $C_{22}H_{21}NO_3P$ requires 378.1259.

4.3.5. *cis*-2-Carboxy-*N*-diphenylphosphinyl-3-(2-ethylphenyl)aziridine (Table 2, entry 5). Following the general procedure described above *cis*-2*S*,2′*S*,3′*S*-*N*-[(1-diphenylphosphinyl-3-(2-ethylphenyl)-2-aziridinyl)carbonyl]-bornane-10, 2-sultam (118 mg, 0.2 mmol) afforded the product as a colourless oil (51 mg, 65%). $[\alpha]_D^{20}$ −5.7 (*c* 1, $CHCl_3$); IR ν_{max} (CCl_4) 1718, 1439, 1130, 756, 697 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.03 (3H, t, J=7.5 Hz), 2.57 (2H, q, J=7.5 Hz), 3.47 and 4.02 (2H, 2×dd, J_P=15.7 Hz, J=6.6 Hz), 6.66–7.97 (14H, m); δ_C (60 MHz, $CDCl_3$) 15.7, 26.7, 41.8, 42.3, 126.8, 129.2, 129.4, 129.8, 130.3, 130.4, 130.5, 130.6, 132.6, 132.8, 132.9, 133.1, 133.3, 133.4,

134.4, 134.5, 134.6, 144.6, 169.5; MS (CI) *m/z* 348 ([MH−CO_2]$^+$, 100%), 219 (47), 201 (31), 146 (9), 77 (7); HRMS found: [MH−CO_2]$^+$348.1526, $C_{22}H_{22}NOP$ requires 348.1517.

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