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Preparation and Ring-Opening Reactions of *N*-Diphenylphosphinyl Aziridines

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Abstract: Monochiral *N*-Diphenyphosphinyl aziridines ('*N*-Dpp aziridines') may efficiently be prepared from monochiral 2-aminoalcohols. Such aziridines undergo ring-opening reaction with a variety of nucleophiles in good yield. Dephosphinylation is accomplished under mild conditions.

The implementation of aziridine chemistry in organic synthesis has lagged behind that of epoxide chemistry in many respects, despite the obvious similarities between these two classes of strained heterocycles. There are two main reasons for this: firstly, there is a relative dearth of general and simple preparative methods for synthesis of aziridines[2] (in stark contrast to the plethora of methods for epoxide synthesis) and, secondly, the extra valency of nitrogen adds the complication that a suitable masking group need be present; ideally, this group would also activate the three-membered ring to cleavage by nucleophiles. Such activation has most commonly been attained by use of sulfonyl groups, which impart excellent activation for ring-opening processes but suffer from the considerable handicap that they are removed from ring-opened compounds only under harsh conditions.[3] We were interested in such problems for a particular reason, viz. during our previously-documented research programme[4] towards monochiral 3-aminoacids (involving ring-opening of *N*-tosylaziridines by dithiane anions as its fulcrum) we had found that standard desulphonylation protocols had been completely destructive when the nitrogen atom concerned could function as a leaving group. Thus, we sought to replace the problematic sulphonyl group with an alternative species which could function both as a ring-opening activator and be easily detached once ring-cleavage had been attained.

The first possible alternative we examined proved to be succesful (*vide infra*). The diphenylphosphinyl ('Dpp') group, we reasoned, should exhibit a similar activating effect to that shown by a toluenesulphonyl group due the high polarity of the P=O bond, but would be more easily removed due to the lack of interaction of a nitrogen lone pair with phosphorous (X-ray data[5] indicates nitrogen in the diphenylphosphinamide group to be tetrahedral, as opposed to the trigonal nitrogen often observed in the sulfonamide unit). Indeed, Ueki and Ramage had previously shown that Dpp-protection of nitrogen was feasible and that the N-P bond could be cleaved under mild conditions.[6,7] The literature contained few reports of *N*-Dpp aziridines: Cram *et al* had prepared the parent compound (i.e the Dpp aziridine derived from ethylene imine itself) for NMR studies,[8] but there seemed to be no other reports. Thus we embarked on our programme of research by preparing a range of monochiral, 2-amino acid-derived *N*-Dpp aziridines using a method analogous to that we had previously employed to good effect for preparation of *N*-tosylaziridines.[9] Thus, monochiral amino alcohols (**1**)

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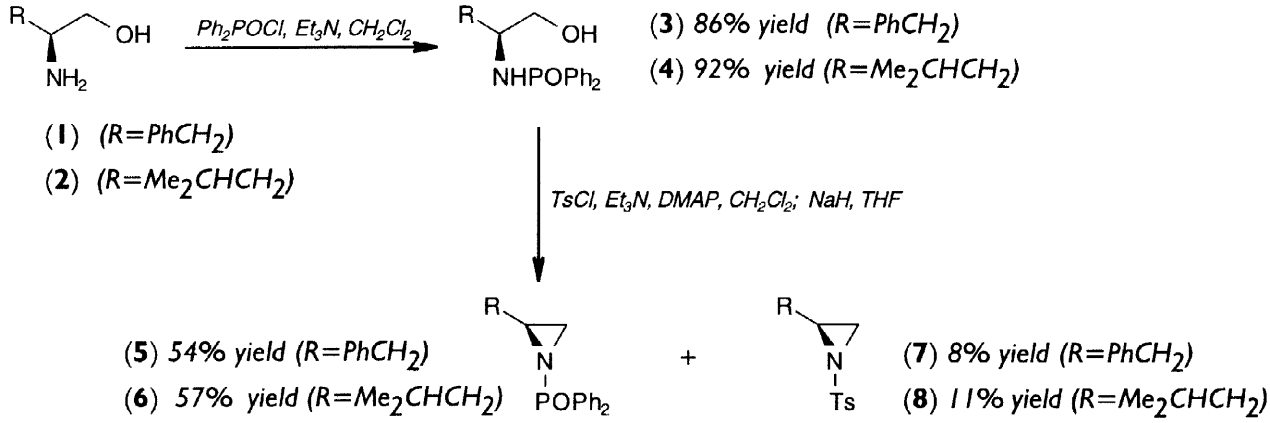
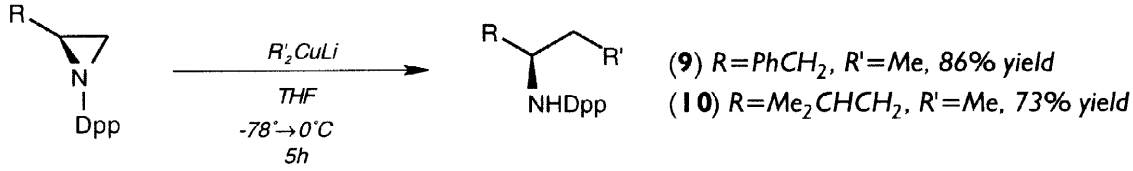
and (**2**), derived from (*S*)-phenylalanine and (*S*)-leucine, respectively, were selectively *N*-diphenylphosphinylated in good yield and the resulting crude phosphinamido alcohols (**3**) and (**4**) were then tosylated. Treatment of these phosphinamidotosylates with triethylamine in refluxing THF (as carried out in synthesis of *N*-tosylaziridines) did not, however, furnish Dpp aziridines and starting materials were returned quantitatively. When a stronger base, sodium hydride, was employed, three-*exo*-tet cyclization smoothly occurred in refluxing THF to give *N*-Dpp aziridines (**5**) and (**6**) in 46% and 52% yields (from aminoalcohols **1** and **2**) (scheme 1). We also isolated a small amount of the corresponding *N*-tosylaziridines (**7**) and (**8**) as by-products. The Dpp aziridines exhibited characteristic long-range P-H coupling in their ^{1}H NMR spectra.



Scheme 1

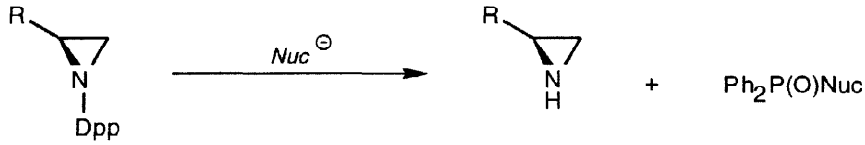
Armed with our proposed new monochiral 2-aminoethyl cation equivalents, we proceeded to the reaction of interest, viz. ring-opening by dithiane anions, but we were disheartened to witness no useful reaction, under a wide range of reaction conditions, between either aziridine (**5**) or (**6**) and a range of dithiane anions which had previously proved useful in ring-opening of *N*-tosylaziridines. In these reactions, a plethora of products were observed, none of which corresponded to the desired ring-opened product and the majority of which evaded identification. The use of di(phenylsulphonyl)methane anions (previously used as effective alternatives where use of dithiane anions had been fruitless) improved the situation in as much as the reactions did not deliver complex mixtures of unidentifiable products, but the only compounds isolated from the reactions were starting materials. The reaction of our Dpp aziridines with dimethylcopperlithium gave the first indication that phosphorous activation of aziridines might prove synthetically useful: ring-opening occured smoothly and cleanly to give the ring-opened product arising from attack of nucleophile at the aziridine carbon atom of lesser substitution to give *N*-Dpp amines (**9**) and (**10**) in good yield (86% and 73%, respectively).



Scheme 2

When we attempted to extrapolate this observation by using a range of alkyl and aryl cuprates, we were once more disappointed to observe no ring-opening reaction taking place. In this case, the organometallic reagents nucleophilically attacked phosphorous, rather than carbon, and dephosphinylation was observed, giving the apposite alkyl or aryl diphenylphosphine oxides (**11**) and (**13**) in moderate yield (Table 1). This is, of course, a laborious way of preparing such compounds, but the reaction parallels that of *N*-acylaziridines, which frequently function as acylating agents.[10] The use of higher order cuprates did not alleviate the problem and alkyl lithiums reacted in similar fashion. Reaction with EtMgBr yielded neither the product of ring-opening, nor the product arising from attack at phosphorous, even when the reaction was carried in refluxing THF. Only starting materials were isolated from the reaction. The use of sulphur-stabilized copper(I) additives (such as $CuBr.SEt_2$ or $CuBr.SMe_2$) at temperatures between -40 and 0°C also returned starting materials as the only product of the reactions.

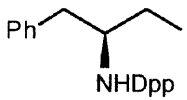
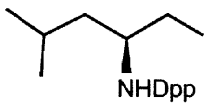
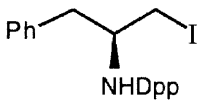
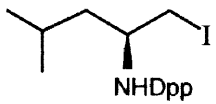
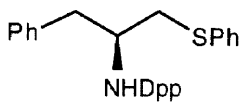
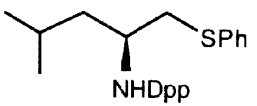
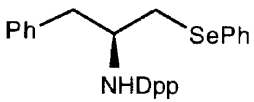
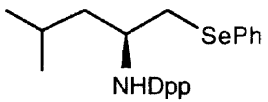
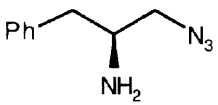
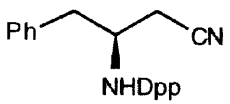
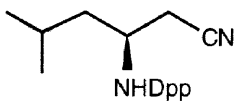
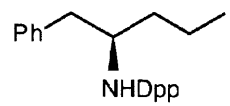
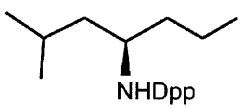
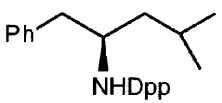
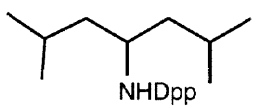
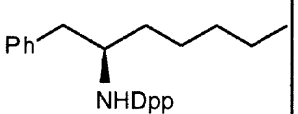
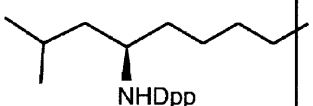
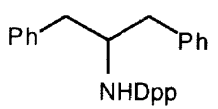
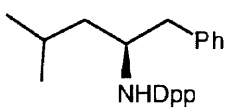
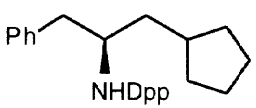
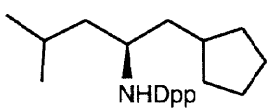
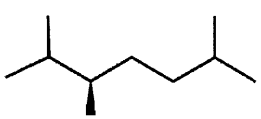
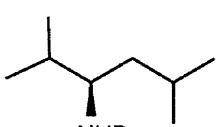
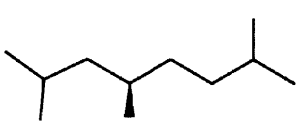
TABLE 1 - DEPHOSPHINYLATION OF *N*-DPP AZIRIDINES



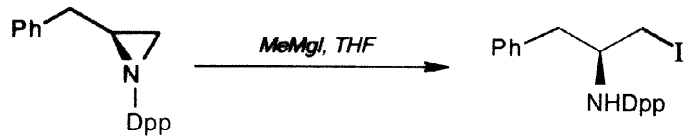
R	Conditions	Product	Yield/%
Bn	Bu_2CuLi, THF, -78°C to 0°C, 2h	$Ph_2P(O)Bu$ (**11**)	61
^iBu	Bu_2CuLi, THF, -78°C to 0°C, 2h	$Ph_2P(O)Bu$ (**11**)	83
^iBu	$BuLi,Ce(III)Cl_3$, THF, -78°C, 2h	$Ph_2P(O)Bu$ (**11**)	80
$PhCH_2$	MeOH, BF_3OEt_2, 0°C, 4h	$Ph_2P(O)OMe$ (**12**)	99
^iBu	MeOH, BF_3OEt_2, 0°C, 2h	$Ph_2P(O)OMe$ (**12**)	65
Bn	PhLi, THF, -78°C, 1.5h	$Ph_2P(O)Ph$ (**13**)	77
^iBu	Ph_2CuLi, THF, -78°C, 2h	$Ph_2P(O)Ph$ (**13**)	76

Thus it seemed that aminoacid-derived Dpp aziridines might, after all, not function as monochiral 2-aminoethyl cation equivalents. The only ring-opening reaction observed with Grignard reagents came when MeMgI caused formation of iodophosphinamide (**14**) (*via in situ* formation of MgI_2) (scheme 3) and, thus we turned our attention to a range of heteroatom-centred nucleophiles and were gratified to witness that these aziridines could, indeed, be ring-opened by such nucleophiles, to give amines (**14**)-(**22**) (Table 2). Successful reaction was observed with azide, phenylsulphanide, phenylselanide, and TMSCN, in addition to the ring-opening reaction with iodide alluded to earlier.

TABLE 2-MONOCHIRAL PHOSPHINAMIDES PREPARED BY NUCLEOPHILIC RING-OPENING OF N-DPP AZIRIDINES

 (9) 86,*§ 67¶	 (10) 73§	 (14) 68	 (15) 77	 (16) 52	 (17) 99
 (18) 92	 (19) 70	 (20) 51	 (21) 56	 (22) 58	 (23) 73†
 (24) 71†	 (25) 88†	 (26) 84†	 (27) 89†	 (28) 76†	 (29) 93†
 (30) 76†	 (31) 53†	 (32) 84†	 (33) 74†	 (34) 56†	 (35) 60†

*Isolated yield of phosphinamide/%. §Me_2CuLi used as nucleophile; ¶MeMgBr used as nucleophile; †appropriate Grignard reagent used in presence of $CuBr.SEt_2$.

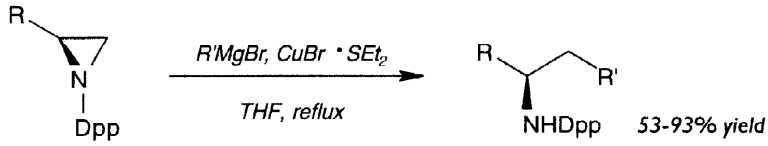


(14)

Scheme 3

The use of methanol in a Lewis acidic environment, however, yielded only methyl diphenylphosphinite (**12**), the product of attack at phosphorous in analogous fashion to the reaction of the variety of organometallic species mentioned before. These data encouraged us in our belief that Dpp aziridines could undergo efficient ring-opening reactions and, indeed, we were pleased to observe that the ammonium chloride-catalyzed ring-opening by azide furnished only an ***amine*** (**20**) rather than a phosphinamide product. In other words, the Dpp group had been cleaved during the reaction (and might have been removed prior to reaction, thereby accounting for the low yield we obtained), demonstrating in a categoric fashion the mild conditions required for its removal. An *in situ* deprotection under these timid reaction conditions is unheard in the chemistry of *N*-sulfonylaziridines.

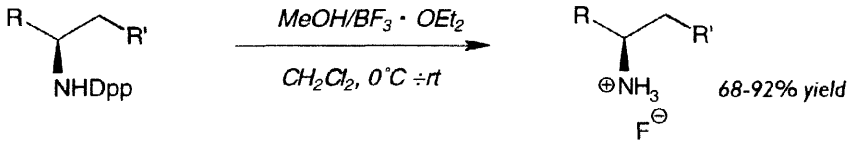
To offer a realistic alternative as an aziridine activator, however, we had to address the lack of ***general*** reactivity shown by Dpp aziridines when confronted with carbon-centred nucleophiles. As previously stated, the use of Grignard reagents was unproductive with regard to alkylative ring-cleavage, even in the presence of copper(I) salts at temperatures up to 20°C. When we raised the same copper-mediated reaction to 40°C (at which temperature, many organocopper species are reported to exhibit pronounced instability) smooth ring-opening reaction occurred in good yield. The reaction proved to be general, with aryl and α-branched Grignard reagents also ring-opening Dpp aziridines in good yields to give monochiral amines (**23**)-(**35**) (scheme 4 and Table 2). We can, as yet, offer no explanation for the effectiveness of this reaction under conditions which would normally decompose the nucleophile. The nature of the organometallic species involved is currently under investigation in our laboratories.



Scheme 4

Having demonstrated that Dpp-aziridines could be ring-opened efficiently, we next turned our attention to deprotection. Our first attempts, employing the conditions described by Ramage *et al.*, were unsuccessful, presumably because these conditions were developed for deprotection of 2-aminoacid-derived phosphinamides where the neighbouring carboxyl group exerts an accelerating influence on the rate of the reaction. Thus, we turned to the Lewis acid-promulgated methanolysis reaction we had earlier observed when attempting ring-opening reactions and confirmed that these conditions could, indeed, be used to effect dephosphinylation. The general process involved treatment of phosphinamide with excess boron trifluoride etherate and methanol in CH_2Cl_2 at room temperature overnight. Acid washing of the product allowed removal of the phosphinate by-product by a simple extraction and furnished the amine in aqueous solution as the hydrofluoride salt. This

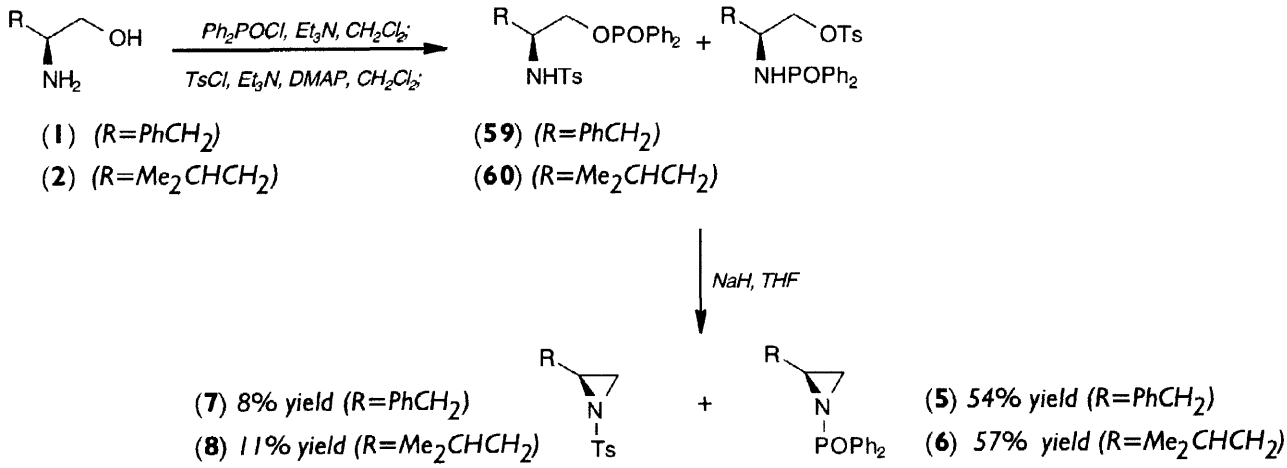
aqueous layer could be freeze-dried to give the hydrofluoride salts (**36**)-(**58**) in essentially pure form, usually greater then 80% (scheme 5); if desired, the free amine could be obtained by basification. These data are summarized in Table 3.



Scheme 5

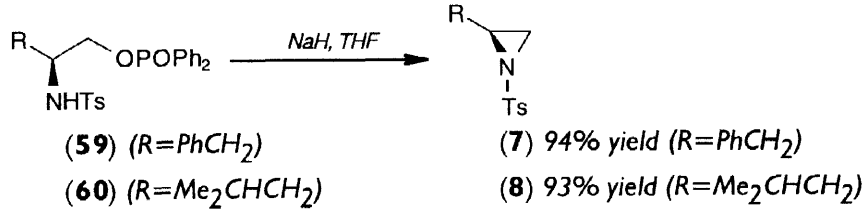
OPTIMIZATION OF DPP AZIRIDINE SYNTHESIS

As mentioned, when we prepared our first Dpp aziridines (**5**) and (**6**) we always obtained small amounts of the corresponding *N*-tosyl aziridines (**7**) and (**8**). These compounds, we later reasoned, could only have been formed from sulphonamido phosphinites (**59**) and (**60**) (scheme 6) (which could be separated from their isomers by flash chromatography), which presumably arose from an *in situ* O→N Dpp migration.



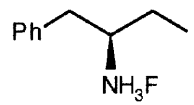
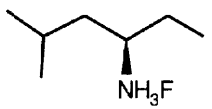
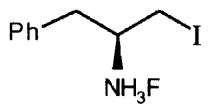
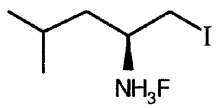
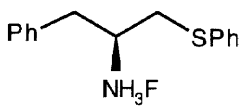
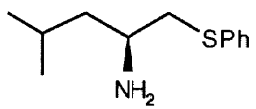
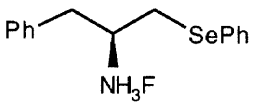
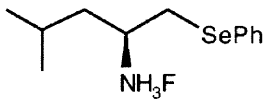
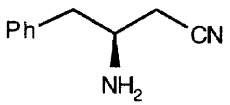
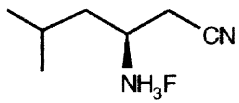
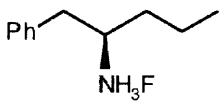
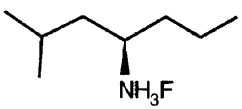
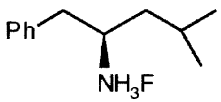
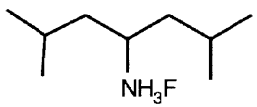
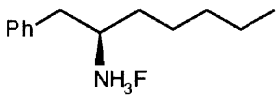
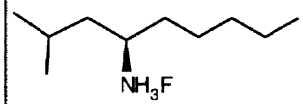
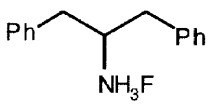
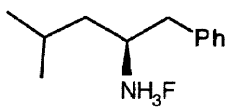
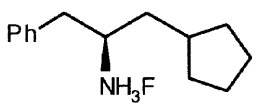
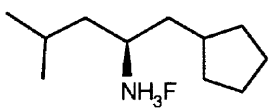
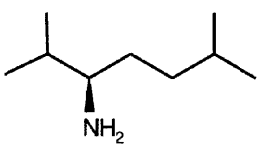
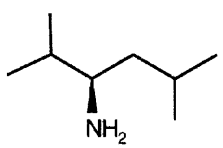
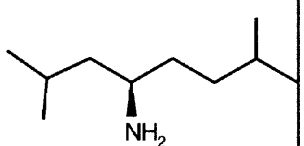
Scheme 6

This realization led us to conclude that a diphenylphosphinite leaving group must be sufficiently nucleofugal to participate in an S_N2 displacement reaction, which immediately led us to the notion of a 'one-pot' preparation of Dpp aziridines. Indeed, when pure (**59**) and (**60**) were exposed to the conditions previously used for cyclization, an excellent yield of *N*-tosyl aziridines (**7**) and (**8**) was obtained, reinforcing our proposal (scheme 7).



Scheme 7

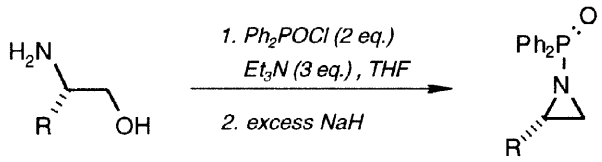
TABLE 3-DEPROTECTION OF PHOSPHINAMIDES

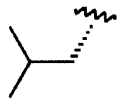
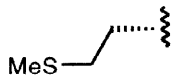
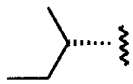
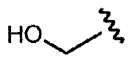
 **(36)** 87#	 **(37)** 80	 **(38)** 84	 **(39)** 81	 **(40)** 85	 **(41)** 76
 **(42)** 92	 **(43)** 88	 **(44)** 89	 **(45)** 89	 **(46)** 73	 **(47)** 76
 **(48)** 82	 **(49)** 77	 **(50)** 79	 **(51)** 80	 **(52)** 91	 **(53)** 89
 **(54)** 68	 **(55)** 85	 **(56)** 85	 **(57)** 85	 **(58)** 85	

*Dpp = diphenylphosphinyl; [§]Me_2CuLi used as nucleophile; [¶]MeMgBr used as nucleophile; #Isolated yield of amine in %.

The notion of the method allowing a 'one-pot' preparation of *N*-Dpp aziridines was realized in practice by treating monochiral aminoalcohols with two equivalents of diphenylphosphinic chloride in the presence of triethylamine, and treating the crude *bis*phosphinylated products between 0°C and room temperature with sufficient excess sodium hydride to neutralize the triethylammonium hydrochloride formed during the reaction and effect cyclization. Under these conditions, a variety of monochiral Dpp aziridines were prepared efficiently (table 4). This method represents a highly efficient synthesis of these new reagents.

TABLE 4- PREPARATION OF *N*-DIPHENYLPHOSPHINYL AZIRIDINES FROM AMINOALCOHOLS



R	Yield of aziridine/%
Bn	(**5**), 86
	(**6**), 78
	(**61**), 67
Ph	(**62**), 52
Me	(**63**), 56
	(**64**), 79
	(**65**), 87
	(**66**), 60

CONCLUSION

We have prepared the first monochiral *N*-diphenylphosphinyl aziridines and demonstrated that they undergo ring-opening reactions with a range of heteroatom- and carbon-centred nucleophiles. The products of these ring-openings undergo dephosphinylation under comparatively mild conditions, thereby offering a useful practical alternative to the use of sulfonamide activation of aziridines.

ACKNOWLEDGEMENT

We acknowledge the financial support of the EPSRC (CASE award to AAC), Parke Davis Neuroscience Research Centre (Cambridge, UK) (studentship award to HMIO), the University of Bristol, the Nuffield Foundation and ZENECA (for an award from the Strategic Research Fund to JBS).

EXPERIMENTAL

General Techniques

All organic solvents were distilled prior to use and all reagents were purified by standard procedures. Light petroleum refers to the fraction with the boiling range 40°C to 60°C. Diethyl ether, THF and DME were distilled from sodium benzophenone ketyl; toluene from sodium; dichloromethane, triethylamine, di-isopropylamine and acetonitrile from calcium hydride, and pyridine and di-isopropylethylamine from potassium hydroxide.

Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer 881 spectrophotometer. Optical rotations were measured using a Perkin Elmer 241MC polarimeter and are quoted in 10^{-1} deg cm^2 g^{-1}. Mass spectra were recorded on a VG9090 mass spectrometer or on a Fisons Autospec machine. ^1H and ^{13}C nmr spectra were recorded on a Jeol GX-270 spectrometer or a Jeol L-300 spectrometer. Unless otherwise stated, deuterochloroform was used as solvent and tetramethylsilane was used as the internal standard. Chemical shifts in ^1H nmr spectra are expressed as ppm downfield from tetramethylsilane, and in ^{13}C nmr, relative to the internal solvent standard. Coupling constants are quoted in Hz. ^{31}P spectra were recorded using a JEOL GX-400 spectrometer with chemical shifts reported relative to H_3PO_4.

Reactions involving chemicals or intermediates sensitive to air and / or moisture were performed under a nitrogen atmosphere in flame- or oven-dried apparatus. Flash column chromatography[203] was performed using Merck kieselgel 60 or Fluka kieselgel 60 silica. Analytical thin layer chromatography (tlc) was performed on precoated Merck kieselgel 60 F_{254} aluminium backed plates and were visualised under U.V. conditions at 254 nm, and by staining with an acidic ammonium molybdate spray.

*General method for the N-phosphinylation of amino alcohols (**1**) and (**2**)*

To a solution of the amino alcohol (1 equivalent) in CH_2Cl_2, under N_2, at 0 °C, was added DppCl (1 equivalent) and Et3N (1 equivalent). The solution was stirred at 0 °C for 1 hour, then at room temperature for 4 hours. The solution was then partitioned between CH_2Cl_2 and H_2O, the aqueous layer extracted with CH_2Cl_2, the organic layers washed with brine, dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to leave the *N*-Dpp amino alcohols which were used without further purification.

(S)-2-(Diphenylphosphinamido)-3-phenylpropan-1-ol (**3**). By following the general procedure described above amino alcohol (**1**) (0.20g, 1.32 mmol), diphenylphosphinic chloride (0.25 ml, 1.32 mmol) and Et3N (0.18 ml, 1.32 mmol) in CH_2Cl_2 (15 ml) were reacted to yield alcohol (**3**) (0.40g, 86%) as a clear oil. R_f 0.05 (ethyl acetate); $[\alpha]_D^{23}$ -30.23, (*c* 13 in CH_2Cl_2); ν_{max} (neat liquid) / cm^{-1} 3350 (OH), 2940 (NH and CH), 1580 (P=O), 1445 (P=O), 1180 (P=O), 1040, 980; δ_H (270 MHz, $CDCl_3$) 2.73 (1H, dd, *J* 9.0, 13.5, C<u>H</u> of C<u>H</u>2Ph), 2.88 (1H, dd, *J* 2.5, 13.5, C<u>H</u> of C<u>H</u>2Ph), 3.02-3.19 (1H, m, br, N<u>H</u>), 3.60 (1H, dd, *J* 6.0, 11.5, C<u>H</u> of

CH_2OH), 3.71-3.82 (2H, m, CH and one CH of CH_2OH), 4.07-4.89 (1H, s, br, OH), 7.05-7.52 and 7.70-7.83 (15H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 39.21 (d, J 8.5, $PhCH_2$), 56.13 (CH), 65.78 (CH_2OH), 127.83, 127.99, 129.37, 131.10, 131.30, 131.45, 132.08, 138.50 (ArC); m / z (EI) 320 (M-CH_2OH, 32%), 120 (100), 120 (49), 91 (29) and 77(34); Found 320.1200. $C_{20}H_{19}NOP$ requires 320.1204.

(S)-2-(Diphenylphosphinamido)-4-methyl-pentan-1-ol (**4**). By following the general procedure described above (S)-(+)-leucinol (**2**) (0.3g, 2.6 mmol), diphenylphosphinic chloride (0.55 ml, 2.6 mmol) and Et_3N (0.36 ml, 2.6 mmol) in CH_2Cl_2 (15 ml) were reacted to yield alcohol (**4**) (0.76g, 92%) as a clear oil. R_f 0.05 (ethyl acetate); $[\alpha]_D^{23}$ -26 (c 24 in CH_2Cl_2); ν_{max} (neat liquid) / cm^{-1} 3400 (OH), 2960 (NH and CH), 1600 (P=O), 1438 (P=O), 1125 (P=O); δ_H (270 MHz, $CDCl_3$) 0.72 and 0.82 (6H, 2 x d, J 6.5, Me_2CH), 1.32-1.48 (2H, m, Me_2CHCH_2), 1.66-1.79 (1H, m, Me_2CH), 3.05-3.13 (1H, m, Me_2CHCH_2CH), 3.65 (1H, dd, J 2.5, 11.5, CH of CH_2OH), 3.71-3.99 (2H, m, CH of CH_2OH and NH), 4.08-4.25 (1H, s, br, OH), 7.30-7.51 and 7.74-7.93 (10H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 21.98 and 22.55 (Me_2CH), 24.24 (Me_2CH), 42.50 (d, J 9.5, Me_2CHCH_2), 52.68 (CH_2OH), 66.73 (CH), 127.92, 127.99, 128.13, 128.32, 131.42, 131.56, 132.10, 132.24 (ArC); m / z (EI) 318 (M+1, 10%), 286 (M-CH_2OH, 98), 201 (100) and 77 (54); Found 286.1370. $C_{17}H_{21}NOP$ requires 286.1361.

General method for the formation of N-diphenylphosphinyl aziridines (**5**) *and* (**6**)

To a solution of the *N*-Dpp alcohol (**3**) or (**4**) in CH_2Cl_2, under N_2, at 0°C, was added TsCl (1.1 equivalents), DMAP (0.1 equivalents) and Et_3N (3 equivalents), and the solution was allowed to warm to room temperature with stirring overnight. The solution was then poured into aqueous citric acid (2% w / v) and extracted with CH_2Cl_2. The organic layers were then washed with brine, dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to leave a pale yellow residue. To a suspension of NaH (2 equivalents) in THF, under N_2, at 0 °C, was added a solution of this residue in THF. The solution was then allowed to warm to room temperature and stirred for 24 hours. The solution was then partitioned between H_2O and CH_2Cl_2, the aqueous layer extracted with CH_2Cl_2, the organic layers washed with brine, dried (Na_2SO_4), filtered, and the solvent removed *in vacuo* to leave a white solid which was purified by chromatography on silica gel with ethyl acetate-light petroleum (1:1) as eluent.

(S)-N-Diphenylphosphinyl-2-benzyl aziridine (**5**). R_f 0.6 (EtOAc); m.p. 103-105 °C; (Found : C, 74.85; H, 6.08; N, 4.27. $C_{21}H_{20}NPO.0.2\ H_2O$ requires C, 74.85; H, 6.10; N, 4.16%). $[\alpha]_D^{23}$ -7.5 (c 8 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 2988 (CH), 1438, 1391, 1196, 1127 (P=O), 877; δ_H (270 MHz, $CDCl_3$) 2.00 (1H, ddd, J 12.0, 3.5, 1.0, CH of CH_2N), 2.57 (1H, ddd, J 17.5, 6.0, 1.0, CH of CH_2N), 2.84 (2H, d, J 5.5, CH_2Ph), 2.95-3.06 (1H, m, CH), 7.07-7.52 and 7.75-7.94 (15H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 29.20 (d, J 6.5, CH_2), 36.00 (d, J 6.5, CH), 38.64 (d, J 4.5, CH_2), 126.38, 128.15, 128.27, 128.46, 128.69, 131.43, 131.57, 131.69, 133.54, 133.78, 137.67 (ArC); δ_P (161.7 MHz, $CDCl_3$) 32.06; m / z (EI) 333 (M^+, 26%), 242 (8), 201 (69), 132 (100), 91 (31) and 77 (39); Found 333.1284. $C_{21}H_{20}NOP$ requires 333.1283.

(S)-N-Diphenylphosphinyl-2-(2-methylpropyl) aziridine (**6**). R_f 0.4 (ethyl acetate); m.p. 65-66 °C. (Found : C, 72.10; H, 7.53; N, 4.60; P, 9.90. $C_{18}H_{22}NOP$ requires C, 72.22; H, 7.41; N, 4.68; P, 10.35%). $[\alpha]_D^{23}$ -8.7 (c 5 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 2928 (CH), 1438, 1402, 1161, 1126 (P=O); δ_H (270 MHz, $CDCl_3$)

0.76 and 0.83 (6H, 2 x d, *J* 6.5, $\underline{Me_2}CH$), 1.18-1.46 (1H, m, $Me_2\underline{C}H$), 1.50-1.58 (2H, m, $Me_2CH\underline{CH_2}$), **1.92** (1H, ddd, *J* 12.5, 3.5, 1.5, $\underline{C}H$ of $\underline{C}H_2N$), **2.56** (1H, ddd, *J* 17.5, 6.0, 1.5, $\underline{C}H$ of $\underline{C}H_2N$), 2.66-2.78 (1H, m, $\underline{C}H$), 7.28-7.53 and 7.75-7.98 (10H, m, $\underline{Ar}H$); δ_C (67.5 MHz, $CDCl_3$) 21.73 and 22.92 ($\underline{Me_2}CH$), 26.73 ($Me_2\underline{C}H$), 29.96 (d, *J* 7.5, $\underline{C}H_2$), 34.30 (d, *J* 6.5, $\underline{C}H$), 41.68 (d, *J* 4.5, $\underline{C}H_2$), 127.86, 128.11, 128.23, 128.29, 128.40, 131.34, 131.48, 131.54, 131.67, 133.75, 133.89 ($Ar\underline{C}$); δ_P (161.7 MHz, $CDCl_3$) 31.98; m / z (EI) 299 (M^+, 6%), 201 (100), 98 (82), 77 (47) and 42 (66); Found 299.1430. $C_{18}H_{22}NOP$ requires 299.1439.

*Reactions With Nucleophiles Of Aziridines (**5**) And (**6**)*

1. With lower order cuprate reagents. To dry CuI (5 equivalents) in a flame dried flask, under N_2, was added ether (10 ml) and the suspension was degassed by freeze thawing. For the formation of Me_2CuLi the suspension was then cooled to 0° C and MeLi (0.8M, 3.2 ml, 2.56 mmol, 12 equivalents) added dropwise (the solution becomes yellow after the addition of the first equivalent of MeLi, colourless after the addition of the second equivalent). For the formation of Ph_2CuLi or Bu_2CuLi the suspension was cooled to -10°C and PhLi or BuLi (12 equivalents) was added dropwise. In all cases the suspension was stirred for 20 minutes prior to further cooling to -78° C. A degassed solution of the aziridine (1 equivalent) in ether (2 ml) was then added dropwise. The solution was stirred at -78° C for 1 hour then at 0° C for 5 hours, after which time it was quenched by the addition of a saturated aqueous solution of NH_4Cl. The solution was partitioned between NH_4Cl (aq) and ether, the aqueous layer extracted with ether (3 x 15 ml), the organic layers washed with brine (30 ml), dried (Na_2SO4), filtered and the solvent removed *in vacuo* to leave a pale yellow oil which was purified by chromatography on silica gel with ethyl acetate-light petroleum (1:1) as eluent

*(R)-1-Phenyl-2-(diphenylphosphinamido)butane (**9**).* By following the general procedure described above aziridine (**5**) (0.07g, 0.21 mmol) and Me_2CuLi, formed from CuI (0.20g, 1.1 mmol) and MeLi (2.6 mmol), in ether (10 ml) were reacted to yield (**9**) as a white solid (0.065g, 86%). R_f 0.3 [ethyl acetate-light petroleum (1:1)]; m.p. 121-122° C; (Found : C, 75.32; H, 6.72; N, 3.75. $C_{22}H_{24}NPO$ requires C, 75.62; H, 6.92; N, 4.01%). $[\alpha]_D^{23}$ -1, (*c* 5 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3366 (NH), 3060, 2964 (CH), 1598, 1438, 1208, 1124 (P=O), 878, 698; δ_H (270 MHz, $CDCl_3$) 0.98 (3H, t, *J* 7.3, $\underline{Me}CH_2$), 1.53-1.63 (2H, m, $C\underline{H_2}CH_3$), 1.80-2.02 (1H, m, $N\underline{H}$), 2.80 (1H, dd, *J* 6.5, 13.5, $\underline{C}H$ of $\underline{C}H_2Ph$), 2.89 (1H, dd, *J* 13.5, 5.5, $\underline{C}H$ of $\underline{C}H_2Ph$), 3.16-3.28 (1H, m, $\underline{C}H$), 7.08-7.93 (15H, m, $\underline{Ar}H$); δ_C (67.5 MHz, $CDCl_3$) 10.17 ($\underline{Me}$), 29.34 (d, *J* 4.3, $\underline{C}H_2$), 42.45 (d, *J* 5.4, $\underline{C}H_2$), 54.44 ($\underline{C}H$), 126.34, 128.30, 128.45, 128.50, 129.88, 131.54, 131.70, 132.05, 132.13, 132.18, 132.26, 138.46 (ArC); δ_P (161.7 MHz, $CDCl_3$) 21.45; m / z (CI) 378 (M+29, 11%), 350 (M+1, 61), 320 (10), 258 (100), 201 (40) and 91 (14); Found: 350.1673. $C_{22}H_{25}NOP$ requires 350.1674.

*(R)-2-Methyl-4-(diphenylphosphinamido)hexane (**10**).* By following the general procedure described above aziridine (**6**) (0.1g, 0.33 mmol) and Me_2CuLi, prepared from CuI (0.32g, 1.7 mmol) and MeLi (4.0 mmol) were reacted in ether (10 ml) at 0°C to yield (**10**) (0.08g, 73%) as a white solid. R_f 0.40 (ethyl acetate); m.p.121-122°C; (Found : C, 72.36; H, 8.43; N, 4.21. $C_{19}H_{26}NPO$ requires C, 72.36; H, 8.31; N, 4.44%). $[\alpha]_D^{19.5}$ 14.3, (*c* 2 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3366 (NH), 2964 (CH), 1330, 1180 (P=O), 721; δ_H (270MHz, $CDCl_3$) 0.78 and 0.80 (6H, 2 x d, *J* 6.5 and 7.0, $\underline{Me_2}CH$), 0.90 (3H, t, *J* 7.5, $\underline{C}H_3CH_2$), 1.21-1.78 (5H, m, $Me_2C\underline{H}C\underline{H_2}CHC\underline{H_2}CH_3$), 2.62 (1H, dd, *J* 6.0, 10.5, $N\underline{H}$), 2.99-3.10 (1H, m, $\underline{C}H$), 7.40-7.52 and 7.76-7.96 (10H, m, $\underline{Ar}H$); δ_C (67.5 MHz, $CDCl_3$) 9.28 ($\underline{Me}CH_2$), 22.59 and 22.76 ($\underline{Me_2}CH$), 24.66

($Me_2\underline{C}HCH_2$), 29.82 (d, *J* 3.5, $Me_2CH\underline{C}H_2$), 46.10 (d, *J* 5.4, $Me\underline{C}H_2$), 50.84 ($\underline{C}H$), 128.26, 128.45, 131.62, 132.05, 132.19, 132.35 (Ar$\underline{C}$); m / z (CI) 344 (M+29, 18%), 316 (M+1, 100), 286 (93), 258 (70) and 201 (53); Found: 286.1362. $C_{17}H_{21}NOP$ requires 286.1361; Found 258.1039. $C_{15}H_{17}NOP$ requires 258.1048.

P-Butyl-P, P-Bis-phenylphosphine oxide (**11**). By following the general procedure described above for the reaction of aziridines with lower order cuprate reagents, aziridine (**5**) (0.05g, 0.17 mmol) and Bu_2CuLi, formed from CuI (0.16g, 0.84 mmol) and BuLi (0.87 ml, 2.3M, 2.0 mmol), were reacted in ether to yield (**11**) (0.024g, 61%) as a pale brown solid. R_f 0.10 [ethyl acetate-light petroleum (1:1)]; m.p. 85-85.4 °C; ν_{max} (CCl_4) / cm^{-1} 2961 (CH), 1437, 1196, 1120 (P=O), 620; δ_H (270 MHz, $CDCl_3$) 0.89 (3H, t, *J* 7.5, $\underline{Me}CH_2$), 1.38-1.52 (2H, m, $MeC\underline{H}_2$), 1.56-1.69 (2H, m, $MeCH_2C\underline{H}_2$), 2.21-2.32 (2H, m, $MeCH_2CH_2C\underline{H}_2$), 7.43-7.78 (10H, m, Ar$\underline{H}$); δ_C (67.5 MHz, $CDCl_3$) 13.49 ($\underline{Me}CH_2$), 23.41 (d, *J* 3.5, $\underline{C}H_2$), 24.00 (d, *J* 15.0, $\underline{C}H_2$), 29.35 (d, *J* 72.0, $\underline{C}H_2$), 128.62, 130.65, 130.78, 131.53, 132.51 (Ar$\underline{C}$); δ_P (161.7 MHz, $CDCl_3$) ; m / z (EI) 258 (M^+, 14%), 215 (100) and 201 (65); Found 258.1174. $C_{16}H_{19}PO$ requires 258.1173. Compound (**11**) was also produced in 83% when aziridine (**6**) (0.1g, 0.33 mmol) was exposed to the above conditions. When the above experiment was repeated with aziridine (**8**) using 1 equivalent of Bu_2CuLi the same product resulted in comparable yield.

Triphenylphosphine oxide (**13**). By following the general procedure described above for the reaction of aziridines with lower order cuprate reagents, aziridine (**5**) (0.05g, 0.15 mmol) and Ph_2CuLi, formed from CuI (0.14g, 0.75 mmol) and PhLi (1.5 ml, 1M, 1.5 mmol) were reacted in ether to yield (**13**) (0.03g, 76%) as a white solid. m.p. 79-80 °C (lit.,[207] 79-81 °C); δ_H (270 MHz, $CDCl_3$) 7.02-7.77 (ArH); m / z (CI) 279 (M+1, 100%), 201 (31). When the above experiment was repeated using only 1 equivalent of Ph_2CuLi the same product resulted in comparable yields.

2. *Reaction with organolithium species.* To a solution of the aziridine (**5**) (0.05g, 0.15 mmol) in THF (10 ml) under N_2, at -78 °C was added PhLi (0.3 ml, 0.45 mmol) dropwise. The solution was stirred at -78 °C for 1.5 hours afterwhich time H_2O (5 ml) was added. The aqueous layer was then extracted with ether (3 x 15 ml), the organic layers washed with brine (30 ml), dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to leave a pale yellow oil which was purified by chromatography on silica gel with ethyl acetate-light petroleum (1:1) as eluent to give (**13**) (0.032g, 77%) as a white solid. The analytical data for this compound was identical to that recorded above.

Reaction of aziridine (**6**) *with BuLi/CeCl3.* To freshly dried $CeCl_3$ (0.44g, 1.17 mmol), under N_2, was added THF (10 ml) dropwise. The solution was cooled to -78 °C and BuLi (0.59 ml, 1 mmol) added dropwise. The solution was stirred at -78 °C for 1 hour and then a solution of the aziridine (**6**) (0.10g, 0.33 mmol) in THF (2 ml) added dropwise. The solution was stirred at -78 °C for 1 hour. H_2O (5 ml) was then added cautiously and the aqueous layer extracted with ether (3 x 15 ml), the organic layers washed with brine (30 ml), dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to leave a pale yellow oil which was purified by chromatography on silica gel with ethyl acetate as eluent to yield (**11**) (0.068g, 80%) as a pale yellow gum. The analytical data for this compound was identical to that recorded above.

Methyldiphenylphosphonate (12). To a solution of aziridine (**5**) (0.10g, 0.3 mmol) in CH_2Cl_2 (3 ml) under N_2 at 0°C was added MeOH (5 ml) and BF_3OEt_2 (3 drops). The solution was stirred at 0°C to room temperature overnight after which time H_2O (5 ml) was added and the solution extracted with further portions of CH_2Cl_2 (3 x 10 ml). The organic layers were combined, washed with brine (5 ml), dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to leave a yellow gum. This was purified by column chromatography on silica gel with ethyl acetate-light petroleum (1:1) as eluent to yield (**12**) (0.069g, 99%) as a clear oil. R_f 0.2 [ethyl acetate-light petroleum (1:1)]; ν_{max} (oil) / cm^{-1} 2948-2848 (aromatic CH), 1438, 1223, 1129, 1030 (P=O), 799, 754, 730; δ_H (270 MHz, $CDCl_3$) 3.76 (3H, d, *J* 11.0, OCH_3), 7.41-7.56 and 7.77-7.86 (10H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 51.45 (d, *J* 6.5, OCH_3), 128.40, 128.59, 129.89, 131.50, 131.64, 131.91, 132.13, 132.16 (ArC); δ_P (161.7 MHz, $CDCl_3$) 33.18; m / z (EI) 232 (M^+, 54%), 231 (100), 199 (37), 155 (36) and 77 (89); Found 232.0645. $C_{13}H_{13}O_2P$ requires 232.0653.

The above compound (**12**) was also formed in 65% yield by the reaction of aziridine (**6**) (0.10g, 0.34 mmol) with BF_3OEt_2 (3 drops) in MeOH (3 ml) and CH_2Cl_2 (3 ml) under the conditions described above.

3. With MeMgI. To Mg (5 equivalents) in ether (5 ml), at 0°C, under N_2, was added MeI (5.4 equivalents) in ether (1 ml). The solution was stirred at room temperature for 0.5 hour, after which time the formation of MeMgI was complete. The ethereal solution was then added to a solution of the aziridine (**5**) or (**6**) (1 equivalent) in THF (15 ml) at 0°C, causing precipitation of MgI_2. The suspension was stirred at room temperature for 20 hours, after which time the reaction was quenched by the addition of NH_4Cl (sat, aq, 10 ml), and extracted with ether (3 x 20 ml). The organic layers were washed with brine (20 ml), dried (Na_2SO_4), filtered, and the solvent removed *in vacuo* to leave a pale yellow oil.

(S)-1-Iodo-2-(diphenylphosphinamido)-3-phenylpropane (14). By following the general procedure described above aziridine (**5**) (0.10g, 0.30 mmol) and MgI_2, formed from Mg (0.036g, 1.5 mmol) and MeI (0.10 ml, 1.61 mmol) in ether / THF, were reacted to yield (**14**) (0.09g, 68%) as a pale yellow oil. R_f 0.53 (EtOAc); $[\alpha]_D^{23}$ -30.5 (*c* 6 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3363 (NH), 3060, 1438, 1215 (P=O), 1123, 908, 698; δ_H (270 MHz, $CDCl_3$) 2.85-3.05 (3H, m, CH_2Ph plus NH), 3.20-3.24 (1H, m, CH), 3.33 (1H, dd, *J* 10.0, 2.5, CH of CH_2I), 3.50 (1H, dd, *J* 10.0, 5.0, CH of CH_2I), 7.08-7.53 and 7.63-7.88 (15H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 18.03 (CH_2I), 43.05 (d, *J* 6.5, $PhCH_2$), 51.97 (CH), 126.78, 128.37, 128.42, 128.57, 129.40, 131.65, 131.80, 131.94, 132.10, 132.24 (ArC); δ_P (161.7 MHz, $CDCl_3$) 21.90; m / z (EI) 370 (M-$PhCH_2$, 100%), 334 (19), 243 (32) and 201 (97); Found 369.9874. $C_{14}H_{14}NOPI$ requires 369.9858.

(S)-1-Iodo-2-(diphenylphosphinamido)-4-methylpentane (15). By following the general procedure described above aziridine (**6**) (0.10g, 0.33 mmol) and MgI_2, formed from Mg (0.04g, 1.67 mmol) and MeI (0.11ml, 1.79 mmol) in ether / THF were reacted to yield (**15**) (0.17g, 77%) as a pale yellow oil. R_f 0.54 (ethyl acetate); $[\alpha]_D^{23}$ -29.9 (*c* 9 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 2958 (NH), 1438, 1371, 1258, 1215, 1123, 1047 (P=O), 908, 730; δ_H (270 MHz, $CDCl_3$) 0.81 and 0.83 (6H, 2 x d, *J* 6.5, Me_2CH), 1.32-1.52 (2H, m, Me_2CHCH_2), 1.61-1.70 (1H, m, CH), 2.70-2.81 (1H, m, br, NH), 3.09-3.19 (1H, m, CH), 3.39 (1H, dd, *J* 10.0, 2.5, CH of CH_2I), 3.56 (1H, dd, *J* 4.5, 10.0, CH of CH_2I), 7.41-7.55 and 7.69-7.96 (10H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 20.46 (d, *J* 2.1, CH_2I), 22.24 and 22.47 (Me_2CH), 24.33 (Me_2CH), 46.81 (Me_2CHCH_2, d, *J* 6.5), 47.81 (CH), 128.35, 128.38, 128.45, 128.54, 128.57, 128.64, 131.18, 131.59, 131.67, 131.81, 131.96,

132.11, 132.24 (ArC); δ_P (161.7 MHz, $CDCl_3$) 22.11; m / z (EI) 427 (M^+, 3%), 370 (M-57, 61%), 300 (M-I, 52%), 286 (74) and 201 (100); Found: 427.0551. $C_{18}H_{23}NOPI$ requires 427.0562.

4. With lithium thiophenolate. To a solution of thiophenol (3 equivalents) in THF (8 ml), under N_2, at -42°C was added BuLi (3.3 equivalents) dropwise. The solution was stirred at -42°C for 0.5 hours, after which time a solution of aziridine (**5**) or (**6**) (1 equivalent) in THF (1 ml) was added. The solution was gradually warmed up to room temperature and stirred overnight. The solution was then partitioned between H_2O (10 ml) and EtOAc (15 ml), the aqueous layer extracted with EtOAc (2 x 10 ml), the organic layers washed with brine (15 ml), dried (Na_2SO_4), filtered, and the solvent removed *in vacuo* to leave a pale yellow oil which was purified by chromatography on silica gel [ethyl acetate-light petroleum (1:1)].

*(S)-1-Thiophenyl-2-(diphenylphosphinamido)-3-phenylpropane (**16**).* By following the procedure described above aziridine (**5**) (0.06g, 0.18 mmol) and the anion of thiophenol (0.06 ml, 0.54 mmol) were reacted to yield (**16**) (0.41g, 52%) as a clear oil. R_f 0.2 [ethyl acetate-light petroleum (1:1)]; (Found : C, 72.69; H, 6.08; N, 2.97. $C_{27}H_{26}NPOS.0.2H_2O$ requires C, 72.52; H, 5.95; N, 3.13%). $[\alpha]_D^{23}$ -5.8, (*c* 2.4 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3365 (NH), 1207 (P=O); δ_H (270 MHz, $CDCl_3$) 2.93 (1H, dd, *J* 6.5, 13.5, CH of CH_2Ph), 3.01-3.16 (3H, m, NH and CH of CH_2Ph and CH of CH_2SPh), 3.33 (1H, dd, *J* 4.0, 13.5, CH of CH_2SPh), 3.40-3.56 (1H, m, br, CH), 7.03-7.60 and 7.72-7.82 (20H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 39.63 (d, *J* 4.5, $PhCH_2$), 41.37 (d, *J* 5.5, CH_2), 52.48 (CH), 126.00, 126.62, 128.32, 128.40, 128.50, 128.57, 129.00, 129.09, 129.81, 131.83, 131.97, 132.08, 132.21, 135.78, 137.65 (ArC); δ_P (161.7 MHz, $CDCl_3$) 22.30; m / z 443 (M^+, 2%), 352 (M-$PhCH_2$, 38%), 320 (M-$PhSCH_2$, 89%), 218 (50) and 201 (100); Found 443.1472; $C_{27}H_{26}NOPS$ requires 443.1473.

*(S)-1-Thiophenyl-2-(diphenylphosphinamido)-4-methylpentane (**17**).* By following the general procedure described above aziridine (**6**) (0.10g, 0.33 mmol) and the anion of thiophenol (0.11g, 1.00 mmol) were reacted to yield (**17**) (0.13g, 99%) as a clear oil. R_f 0.5 (ethyl acetate); $[\alpha]_D^{23}$ -23.4, (*c* 11 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3361 (NH), 1207 (P=O); δ_H (270 MHz, $CDCl_3$) 0.67 and 0.80 (6H, 2 x d, *J* 6.5, Me_2CH), 1.38-1.48 (1H, m, Me_2CH), 1.54-1.77 (2H, m, Me_2CHCH_2), 2.45 (1H, m, br, NH), 3.06-3.19 (2H, m, CH plus CH of CH_2SPh), 3.37 (1H, dd, *J* 3.5, 14.0, CH of CH_2SPh), 7.11-7.51 and 7.80-7.88 (15H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 22.12 and 22.73 (Me_2CH), 24.55 (Me_2CH), 41.50 (d, *J* 3.0, CH_2), 45.25 (d, *J* 6.5, CH_2), 49.11 (CH), 128.24, 128.29, 128.42, 128.48, 128.88, 129.53, 131.72, 131.80, 131.94, 132.10, 136.10 (ArC); δ_P (161.7 MHz, $CDCl_3$) 21.63; m / z (EI) 409 (M^+, 1%), 286 (M-$PhSCH_2$, 100%), 192 (19), 149 (20), 123 (6) and 77 (23); Found 409.1618. $C_{24}H_{28}NOPS$ requires 409.1629.

5. With sodium phenyl selanide. To a solution of diphenyldiselenide (1.5 equivalents) in ethanol (5 ml), under N_2, at room temperature, was added $NaBH_4$ portionwise(3 equivalents) and stirring was continued until the bright yellow solution became colourless. A solution of aziridine (**5**) or (**6**) (1 equivalent) in THF (3 ml) was then added, at 0°C, and the solution was allowed to warm to room temperature overnight. The solution was then partitioned between H_2O (20 ml) and EtOAc (20 ml), the aqueous layer extracted with EtOAc (2 x 20 ml), the organic layers combined, washed with brine, dried (Na_2SO_4), filtered and the solvent removed *in*

vacuo to leave a yellow oil which was purified by chromatography on silica gel with light petroleum then gradient elution to ethyl acetate-light petroleum (1:1).

(S)-1-Selenophenyl-2-(diphenylphosphinamido)-3-phenylpropane (**18**). By following the general procedure described above aziridine (**5**) (0.10g, 0.30 mmol) and PhSeNa, formed from PhSeSePh (0.14g, 0.45 mmol) and $NaBH_4$ (0.03g, 0.90 mmol), were reacted to yield (**18**) as a pale yellow solid (0.13g, 92%). R_f 0.22 [ethyl acetate-light petroleum (1:1)]; m.p. 124-125°C. (Found : C, 66.13; H, 5.42; N, 2.75; P, 6.09. $C_{27}H_{26}NPOSe$ requires C, 66.12; H, 5.34; N, 2.86; P, 6.32%). $[\alpha]_D^{23}$ -9.4 (*c* 9 in CH_2Cl_2); ν_{max} (neat liquid) / cm^{-1} 3337 (NH), 3167, 2926, 1580, 1477, 1435, 1273, 1181, 1122, 1070 (P=O), 727, 695; δ_H (270 MHz, $CDCl_3$) 2.97 (1H, dd, *J* 6.5, 13.5, C<u>H</u> of C<u>H</u>$_2$Ph), 3.03 (1H, dd, *J* 6.5, 13.5, C<u>H</u> of C<u>H</u>$_2$Ph), 3.09 (1H, dd, *J* 6.5, 12.5, C<u>H</u> of C<u>H</u>$_2$SePh), 3.19 (1H, dd, *J* 6.0, 11.0, N<u>H</u>), 3.29 (1H, dd, *J* 6.5, 12.5, C<u>H</u> of C<u>H</u>$_2$SePh), 3.43-3.56 (1H, m, C<u>H</u>), 7.06-7.57 and 7.72-7.94 (20H, m, Ar<u>H</u>); δ_C (67.5 MHz, $CDCl_3$) 35.14 (d, *J* 4.5, <u>C</u>H$_2$), 42.28 (d, *J* 5.5, <u>C</u>H$_2$), 52.87 (<u>C</u>H), 126.51, 126.83, 128.24, 128.30, 128.42, 128.50, 129.15, 129.69, 131.56, 131.59, 131.67, 131.77, 131.91, 132.02, 132.16, 132.32, 137.80 (Ar<u>C</u>); δ_P (161.7 MHz, $CDCl_3$) 21.80; m / z (EI) 491 (M+1, 3%), 400 (44), 201 (100), 91 (44) and 77 (31); Found 491.0926. $C_{27}H_{26}NPOSe$ requires 491.0917.

(S)-1-Selenophenyl-2-(diphenylphosphinamido)-4-methylpentane (**19**). By following the general procedure described above aziridine (**6**) (0.10g, 0.33 mmol) and PhSeNa, formed from PhSeSePh (0.16g, 0.50 mmol) and $NaBH_4$ (0.04g, 1.0 mmol), were reacted to yield (**19**) as a clear oil (0.11g, 70%). R_f 0.3 (ethyl acetate); (Found : C, 63.02; H, 6.37; N, 3.52. $C_{24}H_{28}NPO$ requires C, 63.16; H, 6.18; N, 3.07%). $[\alpha]_D^{23}$ -16 (*c* 6 in CH_2Cl_2); ν_{max} (neat liquid) / cm^{-1} 3167 (NH), 1580, 1435 (P=O), 1181 (P=O), 666 (ArH); δ_H (270 MHz, $CDCl_3$) 0.76-0.77 (6H, 2 x d, *J* 6.5, <u>Me</u>$_2$CH), 1.21-1.26 (1H, m, Me$_2$C<u>H</u>), 1.38-1.70 (2H, m, Me$_2$CHC<u>H</u>$_2$), 3.18 (1H, dd, *J* 6.5, 13.0, C<u>H</u> of C<u>H</u>$_2$SePh), 3.34 (1H, dd, *J* 13.0, 3.0, C<u>H</u> of C<u>H</u>$_2$SePh), 3.40-3.49 (2H, m, Me$_2$CHCH$_2$C<u>H</u>N<u>H</u>Dpp), 7.36-7.53 and 7.73-7.97 (15H, m, Ar<u>H</u>); δ_C (67.5 MHz, $CDCl_3$) 22.27 and 22.52 (<u>Me</u>$_2$CH), 24.65 (Me$_2$<u>C</u>H), 41.76 (d, *J* 4.5, <u>C</u>H$_2$), 46.06 (d, *J* 6.5, <u>C</u>H$_2$), 49.21 (<u>C</u>H), 126.89, 128.16, 128.26, 128.34, 128.45, 129.08, 131.34, 131.53, 131.61, 131.73, 131.80, 131.94, 132.11, 132.26, 132.75 (Ar<u>C</u>); m / z (EI) 457 (M^+, 6%), 286 (100), 218 (33) and 201 (96); Found: 457.1065. $C_{24}H_{28}NOPSe$ requires 457.1074.

6. With azide anion

(S)-1-Azido-3-phenyl-propan-2-amine (**20**). To a solution of aziridine (**5**) (0.10g, 0.30 mmol) in EtOH-H_2O (12 ml, 3:1) was added NaN_3 (0.06g, 0.90 mmol, 3 equivalents) and NH_4Cl (0.05g, 0.90 mmol, 3 equivalents). The solution was then heated under reflux for 5 hours, after which time the solution was partitioned between CH_2Cl_2 and H_2O, the aqueous layer extracted with CH_2Cl_2 (2 x 15 ml), the combined organic layers washed with brine (20 ml), dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. The crude product was then purified by chromatography on silica gel with EtOAc as the eluent to leave (**20**) as a clear oil (0.06g, 51%); R_f 0.1 (EtOAc); $[\alpha]_D^{23}$ 17.4 (*c* 2 in CH_2Cl_2);.ν_{max} (CCl_4) / cm^{-1} 3386 (NH), 2921, 2103 (N_3), 1603, 1493, 1445 (P=O), 1277, 1127, 699; δ_H (270 MHz, $CDCl_3$) 1.40-1.43 (2H, m, br, N<u>H</u>$_2$), 2.59 (1H, dd, *J* 7.5, 13.5, C<u>H</u> of C<u>H</u>$_2$Ph), 2.80 (1H, dd, *J* 4.5, 13.5, C<u>H</u> of C<u>H</u>$_2$Ph), 3.20-3.26 (2H, m, C<u>H</u> and C<u>H</u> of C<u>H</u>$_2$N$_3$), 3.40 (1H, dd, *J* 5.5, 13.0, C<u>H</u> of C<u>H</u>$_2$N$_3$), 7.07-7.36 (5H, m, Ar<u>H</u>); δ_C (67.5 MHz, $CDCl_3$)

52.38 (CH), 56.92 (CH_2), 65.83 (CH_2), 126.67, 128.65, 129.18, 137.81 (ArC); m / z (EI) 149 ($M\text{-}N_2^+$, 18%), 132 (38), 120 (28), 91 (42), 84 (69) and 49 (100).

7. With TMSCN. To freshly dried $CeCl_3$ (0.25 equivalents), under N_2, was added THF (7 ml) and the solution was cooled to -78°C. BuLi (0.75 equivalents) was then added dropwise and the yellow solution allowed to stir at -78°C for 15 minutes. TMSCN (2 equivalents) was added dropwise, followed by a solution of aziridine (**5**) or (**6**) (1 equivalent) in THF (1 ml). The solution was then heated under reflux for 4 hours, after which time H_2O (20 ml) was added to the cooled solution. The solution was then extracted with ether (3 x 25 ml), the organic layers washed with brine (30 ml), dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to leave a brown oil which was purified by chromatography on silica gel with EtOAc as eluent to leave the required product as a pale brown oil.

(S)-1-Cyano-2-(diphenylphosphinamido)-3-phenylpropane (**21**). By following the general procedure described above aziridine (**5**) (0.10g, 0.30 mmol), TMSCN (0.09ml, 0.68 mmol) and $Ce(CN)_3$ (0.08 mmol) were reacted to yield (**21**) (0.06g, 56%) as a pale brown oil. R_f 0.20 (EtOAc); $[\alpha]_D^{23}$ -12 (*c* 5 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3165 (NH), 3060, 2926 (CH), 2248 (CN), 1437, 1263, 1218, 1126, 1045, 700; δ_H (270MHz, $CDCl_3$) 2.43 (1H, dd, *J* 4.0, 16.5, CH of CH_2Ph), 2.66 (1H, dd, *J* 16.5, 5.5, CH of CH_2Ph), 2.84 (1H, dd, *J* 6.5, 13.5, CH of CH_2CN), 2.91 (1H, dd, *J* 13.5, 6.5, CH of CH CN), 3.13 (1H, dd, *J* 6.5, 11.0, NH), 3.37-3.50 (1H, m, CH), 7.01-7.50 and 7.64-7.73 (15H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 25.66 (CH_2), 42.12 (d, *J* 7.5, CH_2), 49.59 (CH), 117.49 (CN), 127.19, 128.50, 128.58, 128.70, 128.76, 128.83, 129.43, 131.57, 131.72, 132.08, 132.24, 132.91, 136.46 (ArC); δ_P (161.7 MHz, $CDCl_3$) 23.14; m / z (EI) 360 (M^+, 3%), 320 ($M\text{-}CH_2CN$, 13), 269 ($M\text{-}PhCH_2$, 71), 201 (100), 91 (20) and 77 (26); Found 360.1392. $C_{22}H_{21}N_2OP$ requires 360.1392.

(S)-1-Cyano-2-(diphenylphosphinamido)-4-methylpentane (**22**). By following the general procedure described above aziridine (**6**) (0.10g, 0.33 mmol), TMSCN (0.09ml, 0.68 mmol) and $Ce(CN)_3$ (0.08 mmol) were reacted to yield (**22**) (0.06g, 58%) as a pale brown oil. R_f 0.39 (ethyl acetate); $[\alpha]_D^{20}$ -4.1 (*c* 5.8 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 2871 (CH and NH), 2247 (CN), 1598, 1437, 1208, 1125, 1031, 870; δ_H (270 MHz, $CDCl_3$) 0.81 and 0.86 (6H, 2 x d, *J* 6.5 and 6.5, Me_2CH), 1.35-1.83 (3H, m, Me_2CHCH_2), 2.56 (1H, dd, *J* 3.5, 16.5, CH of CH_2CN), 2.86 (1H, dd, *J* 5.5, 16.5, CH of CH_2CN), 3.11-3.18 (1H, m, NH), 3.36-3.48 (1H, m, CH), 7.43-7.57 and 7.83-7.94 (10H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 21.98 and 22.57 (Me_2CH), 24.55 (Me_2CH), 26.76 (Me_2CHCH_2), 45.37 (d, *J* 7.5, CH_2CN), 45.95 (CH), 117.56 (CN), 128.53, 128.57, 128.70, 128.76, 131.57, 131.72, 132.15, 132.23, 132.29 (ArC); δ_P (161.7 MHz, $CDCl_3$) 22.81; m / z (EI) 326 (M^+, 10%), 286 (M-CN, 66), 269 (24), 201 (100) and 77 (28); Found: 326.1545. $C_{19}H_{23}N_2OP$ requires 326.1548.

8. General Method for copper-catalysed Grignard reactions. To $CuBr.SEt_2$ (2 mol%), under N_2, at room temperature was added a solution of *N*-Dpp aziridine (**5**) or (**6**) in THF (typically 0.3 mmol in 5 ml THF). The solution was then cooled to -40°C and a solution of Grignard reagent in THF added dropwise (5 equivalents). The solution was warmed to room temperature over 10 minutes and then heated under reflux until tlc indicated the reaction to have gone to completion (typically 4 hours). The reaction was then quenched by the

addition of a saturated aqueous solution of NH_4Cl (5 ml), and the aqueous layer extracted with EtOAc (3 x 15 ml). The combined organic layers were washed with brine (10 ml), dried (Na_2SO_4), filtered and the solvent removed *in vacuo*. The products were purified by column chromatography using EtOAc as the eluting solvent.

(R)-1-Phenyl-2-(diphenylphosphinamido)butane ***(9)***. By following the general procedure described above aziridine (**5**) (0.1g, 0.3 mmol), CuBr.SEt_2 (0.001g, 0.006 mmol) and methyl magnesium bromide (0.75 ml, 2M, 1.5 mmol) were reacted in THF for 4 hours to leave (**9**) (0.07g, 67%) as a white solid. The analytical data obtained for this compound was fully consistent with that reported previously.

(R)-2-Methyl-4-(diphenylphosphinamido)hexane ***(10)***. By following the general method described above aziridine (**6**) (0.1g, 0.33 mmol), CuBr.SEt_2 (0.0011g, 0.007 mmol) and methyl magnesium bromide (0.83 ml, 2M, 1.6 mmol) were reacted in THF for 3 hours to leave (**10**) (0.076g, 73%) as a white solid. The analytical data recorded for this compound was fully consistent with that reported previously.

(R)-1-Phenyl-2-(diphenylphosphinamido)pentane ***(23)***. By following the general procedure described above aziridine (**5**) (0.1g, 0.3 mmol), CuBr.SEt_2 (0.001g, 0.006 mmol) and ethyl magnesium bromide (5 equivalents), prepared from Mg (0.04g, 1.5 mmol) and 1-bromoethane (0.11 ml, 1.5 mmol), were reacted in THF for 4 hours to leave (**23**) (0.08g, 73%) as a white solid. R_f 0.3 (ethyl acetate); m.p. 123-124°C; (Found : C, 76.43; H, 7.44; N, 3.66. $C_{23}H_{26}NPO$ requires C, 76.01; H, 7.21; N, 3.85%). $[\alpha]_D^{19.5}$ -3.03, (*c* 3 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 2900 (NH), 2820 (CH), 1540, 1420, 1190, 1140 (P=O), 715; δ_H (270 MHz, $CDCl_3$) 0.85 (3H, t, *J* 7.5, MeCH_2), 1.21-1.63 (4H, m, MeCH_2CH_2), 2.23-3.04 (3H, m, PhCH_2 and NH), 3.16-3.33 (1H, m, CH), 7.00-7.98 (15H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 13.90 (CH_3), 19.00 (MeCH_2), 38.84 (d, *J* 4.5, PhCH_2CHCH_2), 43.04 (d, *J* 5.5, PhCH_2), 52.89 (PhCH_2CH), 126.24, 126.35, 128.11, 128.23, 128.38, 128.43, 128.57, 128.65, 129.86, 131.40, 131.53, 131.61, 131.65, 132.02, 132.16 (ArC); δ_P (161.7 MHz, $CDCl_3$) 21.33; m / z (CI) 392 (M+29, 25%), 364 (M+1, 100), 334 (47), 272 (98), 201 (73) and 91 (31); Found: 364.1846. $C_{23}H_{27}NPO$ requires 364.1830.

(R)-2-Methyl-4-(diphenylphosphinamido)-heptane ***(24)***. By following the general procedure described above aziridine (**6**) (0.1g, 0.33 mmol), CuBr.SEt_2 (0.0011g, 0.007 mmol) and ethyl magnesium bromide (5 equivalents), prepared from Mg (0.05g, 1.7 mmol) and 1-bromoethane (0.12 ml, 1.5 mmol), were reacted in THF for 4 hours to leave (**24**) (0.08g, 71%) as a white solid. R_f 0.30 (ethyl acetate); m.p. 59-60°C; (Found : C, 71.68; H, 8.49; N, 3.69; P, 9.14. $C_{20}H_{28}NPO.0.25H_2O$ requires C, 71.93; H, 8.60; N, 4.19; P, 9.28%). $[\alpha]_D^{19.5}$ -25.39 (*c* 3.3 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3440 (NH), 3005, 2980 (CH), 1525, 1450, 1240, 1140, 1050 (P=O), 659; δ_H (270 MHz, $CDCl_3$) 0.77 and 0.79 (6H, 2 x d, *J* 6.5 and 6.5, Me$_2$CH), 0.85 (3H, t, *J* 7.5, MeCH_2), 1.24-1.57 and 1.69-1.81 (8H, m, Me$_2$CHCH_2CHCH_2CH_2CH$_3$), 2.60-2.66 (1H, m, NH), 3.03-3.09 (1H, m, Me$_2$CHCH_2CH), 7.27-7.51 and 7.86-7.97 (10H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 14.00 (MeCH_2), 18.33 (MeCH_2), 22.55 and 22.63 (Me$_2$CH), 24.62 (Me$_2$CH), 39.59 (d, *J* 4.5, CH_2), 46.82 (d, *J* 5.5, CH_2), 49.62 (Me$_2$CHCH_2CH), 128.18, 128.37, 131.57, 131.69, 131.81, 131.94, 132.02, 132.13, 132.26, 133.89, 134.04 (ArC); δ_P (161.7 MHz, $CDCl_3$) 21.02; m / z (CI) 358 (M+29, 22%), 330 (M+1, 100), 300 (M-CH_3CH_2, 38), 286 (M-Me$_2$CH, 87), 272 (M-Me$_2$CHCH_2, 73) and 201 (Ph_2PO, 68); Found: 320.1972. $C_{20}H_{29}NPO$ requires 330.1987.

(S)-1-Phenyl-2-(diphenylphosphinamido)-4-methylpentane (**25**). By following the general procedure described above aziridine (**5**) (0.1g, 0.3 mmol), CuBr.SEt$_2$ (0.001g, 0.006 mmol) and isopropyl magnesium bromide (5 equivalents), prepared from Mg (0.04g, 1.5 mmol) and 2-bromopropane (0.14 ml, 1.5 mmol), were reacted in THF for 4 hours to leave (**25**) (0.099g, 88%) as a white solid. R_f 0.5 (ethyl acetate); m.p. 156°C; (Found : C, 75.39; H, 7.69; N, 3.32. $C_{24}H_{28}NPO.0.2H_2O$ requires C, 75.44; H 7.76; N 3.67%). $[\alpha]_D^{19.5}$ -14.70 (*c* 1.7 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3300 (NH), 2860, 2840 (CH), 1510, 1420, 1180, 1140 (P=O); δ_H (270 MHz, $CDCl_3$) 0.74 and 0.81 (6H, 2 x d, *J* 6.5 and 6.5, Me$_2$CH), 1.26-1.47 (2H, m, Me$_2$CHCH$_2$), 1.80-1.90 (1H, m, Me$_2$CH), 2.61 (1H, dd, *J* 5.0, 11.0, NH), 2.86 (1H, dd, *J* 5.5, 13.5, CH of CH$_2$Ph), 2.92 (1H, dd, *J* 6.0, 13.5, CH of CH$_2$Ph), 3.23-3.32 (1H, m, Me$_2$CHCH$_2$CH), 7.14-7.52 and 7.66-7.72 and 7.83-7.91 (15H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 22.38 and 22.66 (Me$_2$CH), 24.62 (Me$_2$CH), 43.35 (d, *J* 4.5, Me$_2$CHCH$_2$), 46.28 (d, *J* 5.5, PhCH$_2$), 51.02 (Me$_2$CHCH$_2$CH), 126.27, 128.24, 130.03, 131.54, 131.57, 131.65, 132.00, 132.16, 132.32, 138.15 (ArC); δ_P (161.7 MHz, $CDCl_3$) 21.14; m / z (CI) 406 (M+29, 16%), 378 (M+1, 82), 286 (M-PhCH$_2$, 100) and 201 (39); Found: 378.1984. $C_{24}H_{29}NPO$ requires 378.1987. The opposite enantiomer, (**30**), was also prepared (0.10g, 76%) by reaction of aziridine (**6**) (0.1g, 0.33 mmol), CuBr.SEt$_2$ (0.0011g, 0.007 mmol) and phenyl magnesium bromide (5 equivalents), prepared from Mg (0.05g, 1.7 mmol) and bromobenzene (0.18 ml, 1.7 mmol), in THF for 4 hours. The analytical data for this compound was identical to that recorded above but for one exception : $[\alpha]_D^{19.5}$ 14.70 (*c* 1.7 in CH_2Cl_2).

2-Methyl-4-(diphenylphosphinamido)-6-methylheptane (**26**). By following the general procedure described above aziridine (**6**) (0.1g, 0.33 mmol), CuBr.SEt$_2$ (0.0011g, 0.007 mmol) and isopropyl magnesium bromide (5 equivalents), prepared from Mg (0.05g, 1.7 mmol) and 2-bromopropane (0.16 ml, 1.7 mmol), were reacted in THF for 4 hours to leave (**26**) (0.10g, 84%) as a white solid. R_f 0.49 (ethyl acetate); m.p. 149-149.3°C; (Found : C, 73.45; H, 8.86; N, 4.05; P, 8.49. $C_{21}H_{30}NPO$ requires C, 73.44; H, 8.80; N, 4.08; P, 9.02%). $[\alpha]_D^{19.5}$ 0 (*c* 3 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3300 (NH), 2960, 2940 (CH), 1540, 1445, 1420, 1385, 1205, 1120 (P=O), 740; δ_H (270 MHz, $CDCl_3$) 0.76 and 0.77 (12H, 2 x d, *J* 6.5 and 6.5, Me$_2$CH), 1.26-1.46 (4H, m, Me$_2$CHCH$_2$), 1.73-1.83 (2H, m, Me$_2$ H), 2.51 (1H, dd, *J* 5.0, 10.5, NH), 2.96-3.08 (1H, m, Me$_2$CHCH$_2$CH), 7.27-7.52 and 7.89-7.97 (10H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 22.59 and 22.66 (Me$_2$CH), 24.63 (Me$_2$CH), 47.64 (d, *J* 5.5, CH$_2$), 48.40 (Me$_2$CHCH$_2$CH), 128.24, 128.42, 131.62, 132.05, 132.21, 132.34 (ArC); δ_P (161.7 MHz, $CDCl_3$) 20.61; m / z (CI) 372 (M+29, 13%), 344 (M+1, 64), 286 (M-Me$_2$CHCH$_2$, 100) and 201 (Ph_2PO).

(R)-1-Phenyl-2-(diphenylphosphinamido)-heptane (**27**). By following the general procedure described above aziridine (**5**) (0.1g, 0.3 mmol), CuBr.SEt$_2$ (0.001g, 0.006 mmol) and butyl magnesium bromide (5 equivalents), prepared from Mg (0.04g, 1.5 mmol) and 1-bromobutane (0.16 ml, 1.5 mmol), were reacted in THF for 4 hours to leave (**27**) (0.10g, 89%) as a white solid. R_f 0.50 (ethyl acetate); m.p. 109°C; (Found : C, 76.50; H, 7.73; N, 3.25. $C_{25}H_{30}NPO$ requires C, 76.70; H, 7.72; N, 3.58%). $[\alpha]_D^{19.5}$ -7 (*c* 1 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 2880 (CH and NH), 1430, 1120 (P=O); δ_H (270 MHz, $CDCl_3$) 0.85 (3H, t, *J* 7.0, MeCH$_2$), 1.08-1.57 (8H, m, MeCH$_2$CH$_2$CH$_2$CH$_2$), 2.67 (1H, dd, *J* 5.5, 11.0, NH), 2.86 (1H, dd, *J* 6.0, 13.5, CH of PhCH$_2$), 2.91 (1H, dd, *J* 5.5, 13.5, CH of CH$_2$Ph), 3.20-3.29 (1H, m, PhCH$_2$CH), 7.03-7.49 and 7.51-7.70 and 7.82-7.90 (15H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 14.01 (CH$_3$), 22.55 (MeCH$_2$), 25.46 (CH$_2$), 31.63 (CH$_2$), 36.62 (d, *J* 4.5, CH$_2$CH), 42.97 (d, *J* 5.5, PhCH$_2$), 53.08 (CH), 126.30, 128.27, 128.45, 129.94, 131.54,

131.67, 132.08, 132.23, 138.40 (ArC); δ_P (161.7 MHz, $CDCl_3$) 21.34; m / z (CI) 420 (M+29, 19%), 392 (M+1, 83), 300 (M-$PhCH_2$, 100) and 201 (51); Found: 392.2133. $C_{25}H_{31}NPO$ requires 392.2143.

(R)-2-Methyl-4-(diphenylphosphinamido)nonane ***(28)***. By following the general procedure described above aziridine (**6**) (0.1g, 0.33 mmol), CuBr.SEt_2 (0.0011g, 0.007 mmol) and butyl magnesium bromide (5 equivalents), prepared from Mg (0.05g, 1.7 mmol) and 1-bromobutane (0.18 ml, 1.7 mmol), were reacted in THF for 4 hours to leave (**28**) (0.10g, 76%) as a white solid. R_f 0.35 (ethyl acetate); m.p. 88-89°C; (Found : C, 73.91; H, 9.32; N, 3.72; P, 9.07. $C_{22}H_{32}NPO$ requires C, 73.92; H, 9.02; N, 3.92; P, 8.66%). $[\alpha]_D^{19.5}$ 24 (*c* 2 CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3500, 3050 (NH), 2980 (CH), 1525, 1490, 1440, 1269, 1180 (P=O), 960, 712; δ_H (270 MHz, $CDCl_3$) 0.77 and 0.80 (6H, 2 x d, *J* 6.5 and 6.5, $\underline{Me}_2CH$), 0.86 (3H, t, *J* 7.0, $\underline{Me}CH_2$), 1.17-1.54 and 1.71-1.79 (11H, m, $Me_2C\underline{H}\underline{C}H_2CHC\underline{H}_2\underline{C}H_2\underline{C}H_2\underline{C}H_2CH_3$), 2.59 (1H, dd, *J* 5.5, 10.5, N$\underline{H}$), 3.00-3.09 (1H, m, $Me_2CHCH_2C\underline{H}$), 7.40-7.52 and 7.87-8.03 (10H, m, Ar$\underline{H}$); δ_C (67.5 MHz, $CDCl_3$) 14.05 ($\underline{Me}CH_2$), 22.59 and 22.74 ($\underline{Me}_2CH$), 24.70 ($Me_2\underline{C}H$), 24.78, 31.78, 37.35 (d, *J* 4.5), 46.78, 46.86 (all $\underline{C}H_2$), 49.82 ($Me_2CHCH_2\underline{C}H$), 128.26, 128.43, 131.64, 132.10, 132.18, 132.24, 132.30 (Ar$\underline{C}$); δ_P (161.7 MHz, $CDCl_3$) 21.01; m / z (CI) 386 (M+29, 19%), 358 (M+1, 97%), 300 (M-Me_2CHCH_2, 78), 286 (M-$MeCH_2CH_2CH_2CH_2$, 100), 201 (Ph_2PO, 59) and 85 (58); Found: 358.2292. $C_{22}H_{33}NPO$ requires 358.2300.

1-Phenyl-2-(diphenylphosphinamido)-3-phenylpropane ***(29)***. By following the general procedure described above aziridine (**5**) (0.1g, 0.3 mmol), CuBr.SEt_2 (0.001g, 0.006 mmol) and phenyl magnesium bromide (5 equivalents), prepared from Mg (0.04g, 1.5 mmol) and bromobenzene (0.16 ml, 1.5 mmol), were reacted in THF for 4 hours to leave (**29**) (0.11g, 93%) as a white solid. R_f 0.44 (ethyl acetate); m.p. 123-124°C; (Found : C, 78.31; H, 6.59; N, 3.42. $C_{27}H_{26}NPO.0.1H_2O$ requires C, 78.46; H, 6.39; N, 3.39%). $[\alpha]_D^{19.5}$ 0 (*c* 3 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3362 (NH and CH), 1556, 1438, 1131 (P=O), 908, 651; δ_H (270 MHz, $CDCl_3$) 2.69 (1H, dd, *J* 4.5, 11.0, N$\underline{H}$), 2.79 (2H, dd, *J* 6.5, 13.5, C$\underline{H}$ of $C\underline{H}_2Ph$), 2.93 (2H, dd, *J* 5.5, 13.5, C$\underline{H}$ of $C\underline{H}_2Ph$), 3.43-3.53 (1H, m, $PhCH_2C\underline{H}$), 7.15-7.55 (20H, m, Ar$\underline{H}$); δ_C (67.5 MHz, $CDCl_3$) 43.63 (d, *J* 4.5, $\underline{C}H_2Ph$), 55.35 ($PhCH_2\underline{C}H$), 127.03, 127.96, 128.63, 128.88, 129.07, 130.62, 132.15, 132.68, 132.84, 139.00 (Ar$\underline{C}$); δ_P (161.7 MHz, $CDCl_3$) 21.53; m / z (CI) 440 (M+29, 30%), 413 (M+2, 50), 412 (M+1, 92), 334 (M-Ph, 26), 320 (M-$PhCH_2$, 100), 201 (Ph_2PO, 68) and 91 (37); Found: 412.1830. $C_{27}H_{27}NPO$ requires 412.1810.

(R)-1-Cyclopentyl-2-(diphenylphosphinamido)-3-phenyl propane ***(31)***. By following the general procedure described above aziridine (**5**) (0.1g, 0.3 mmol), CuBr.SEt_2 (0.001g, 0.006 mmol) and cyclopentyl magnesium bromide (5 equivalents), prepared from Mg (0.04g, 1.5 mmol) and cyclopentyl bromide (0.16 ml, 1.5 mmol), were reacted in THF for 4 hours to leave (**31**) (0.06g, 53%) as a white solid. R_f 0.34 (ethyl acetate); m.p. 118.9-119.7°C; (Found : C, 77.35; H, 7.43; N, 3.58. $C_{26}H_{30}NPO$ requires C, 77.39; H, 7.49; N, 3.47%). $[\alpha]_D^{19.5}$ 12.6 (*c* 2.7 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 2960 (CH and NH), 1540, 1420, 1210, 1130 (P=O), 712; δ_H (270 MHz, $CDCl_3$) 0.74-1.04 and 1.26-1.75 and 1.97-2.08 (11H, m, cyclopentyl and $PhCH_2CHC\underline{H}_2$), 2.64 (1H, dd, *J* 5.5, 11.0, N$\underline{H}$), 2.80 (1H, dd, *J* 6.0, 13.5, C$\underline{H}$ of $C\underline{H}_2Ph$), 3.23 (1H, dd, *J* 13.5, 6.0, C$\underline{H}$ of $C\underline{H}_2Ph$), 3.29-3.31 (1H, m, $PhCH_2C\underline{H}$), 7.08-7.52 and 7.62-7.73 and 7.83-7.91 (15H, m, Ar$\underline{H}$); δ_C (67.5 MHz, $CDCl_3$) 24.98 and 25.03 ($\underline{C}H_2$ of cyclopentyl), 32.64 (d, *J* 5.5, $PhCH_2CH\underline{C}H_2$), 36.68 ($\underline{C}H$ of

cyclopentyl), 43.35 (d, *J* 5.5, PhCH$_2$), 52.40 (PhCH$_2$CH), 126.29, 128.26, 128.45, 130.03, 131.54, 131.57, 131.69, 132.02, 132.18, 132.32, 138.32 (ArC); δ_P (161.7 MHz, $CDCl_3$) 21.27; m / z (CI) 432 (M+29, 5%), 404 (M+1, 27%), 312 (M-PhCH$_2$, 100%) and 201 (42); Found: 404.2130. $C_{26}H_{31}NPO$ requires 404.2140.

(S)-1-Cyclopentyl-2-(diphenylphosphinamido)-4-methylpentane (**32**). By following the general procedure described above aziridine (**6**) (0.1g, 0.33 mmol), CuBr.SEt$_2$ (0.0011g, 0.007 mmol) and cyclopentyl magnesium bromide (5 equivalents), prepared from Mg (0.05g, 1.7 mmol) and cyclopentyl bromide (0.18 ml, 1.7 mmol), were reacted in THF for 4 hours to leave (**32**) (0.10g, 84%) as a white solid. R_f 0.5 (ethyl acetate); m.p. 133-134.5°C; (Found : C, 73.46; H, 8.73; N, 3.48. $C_{23}H_{32}NPO.0.35H_2O$ requires C, 73.51; H, 8.67; N, 3.73%). $[\alpha]_D^{19.5}$ 4.5 (*c* 4.2 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3379 (NH), 3060 (CH), 1438, 1212, 1122 (P=O), 746; δ_H (270 MHz, $CDCl_3$) 0.76 and 0.78 (6H, 2 x d, *J* 6.5 and 6.5, Me$_2$CH), 0.82-1.97 (14H, m, Me$_2$CHCH$_2$CHCH$_2$cyclopentyl), 2.58 (1H, dd, *J* 5.0, 10.5, NH), 2.93-3.06 (1H, m, CH), 7.28-7.52 and 7.88-7.97 (10H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 22.52 and 22.66 (Me$_2$CH), 24.62 (Me$_2$CH), 24.97, 32.67, 32.81 (Cyclopentyl CH$_2$), 36.54 (CH), 44.49 (d, *J* 4.5, CH$_2$), 47.42 (d, *J* 5.5, CH$_2$), 49.51 (Me$_2$CHCH$_2$CH), 128.18, 128.37, 131.54, 131.97, 132.05, 132.13, 132.257, 133.88, 133.97 (ArC); δ_P (161.7 MHz, $CDCl_3$) 20.64; m / z (CI) 398 (M+29, 18%), 370 (M+1, 91), 312 (M-Me$_2$CHCH$_2$, 84), 286 (M-CH$_2$cyclopentyl, 100) and 201 ($POPh_2$, 76); Found: 370.2293. $C_{23}H_{33}NPO$ requires 370.2300.

(R)-2-Methyl-3-(diphenylphosphinamido)-6-methylheptane (**33**). By following the general procedure described before for the reactions of aziridines with copper catalysed Grignard reagents, aziridine (**61**) (1.0g, 3.5 mmol) was reacted with 2-methyl-propane magnesium bromide (17.5 mmol, 5 equivalents) and CuBr.SMe$_2$ (0.014g, 0.07 mmol) in THF for 4 hours to yield (**33**) (0.51g, 74%) as a pale yellow solid. R_f 0.5 (ethyl acetate); m.p. 147-148°C; (Found : C, 73.43; H, 8.82; N, 4.02; P, 8.77. $C_{21}H_{30}NPO$ requires C, 73.44; H, 8.80; N, 4.08; P, 9.02%). $[\alpha]_D^{20}$ -31 (*c* 10 in CH_2Cl_2); ν_{max} (neat liquid) / cm^{-1} 3249 (NH), 2965 (CH), 1447, 1191, 1127 (P=O); δ_H (400 MHz, $CDCl_3$) 0.83-0.87 (9H, m, Me$_2$CH and Me of Me$_2$CH), 0.92 (3H, d, *J* 7.0, Me of Me$_2$CH), 1.02-1.20 and 1.21-1.35 and 1.40-1.55 and 1.80-1.92 (6H, m, Me$_2$CHCH$_2$CH$_2$ and Me$_2$CH), 2.62-2.71 (1H, m, NH), 1.80-1.96 (1H, m, CH), 7.38-7.55 and 7.82-8.00 (10H, m, ArH); δ_C (100 MHz, $CDCl_3$) 17.73, 18.50, 22.50, 22.59, 27.84, 31.14 (d, *J* 4.9, CH$_2$), 32.02 (d, *J* 5.0, CH$_2$), 35.05, 56.73 (CH), 128.15, 128.27, 131.46, 132.05, 132.15, 132.25, 132.72, 134.00 (ArC); m / z (CI) 344 (M+1, 99%), 300 (22), 266 (20), 79 (96), 57 (100). Found 344.2151. $C_{21}H_{31}NOP$ requires 344.2143.

(R)-2-Methyl-3-(diphenylphosphinamido)-5-methylhexane (**34**). By following the general procedure described before for the reactions of aziridines with copper catalysed Grignard reagents, aziridine (**61**) (0.60g, 2.1 mmol) was reacted with *iso*-propyl magnesium bromide (10 mmol, 5 equivalents) and CuBr.SMe$_2$ (0.008g, 0.04 mmol) in THF for 4 hours to yield (**34**) (0.37g, 56%) as a pale yellow solid. R_f 0.4 (ethyl acetate); (Found : C, 72.49; H, 8.39; N, 4.15. $C_{20}H_{28}NPO$ requires C, 72.92; H, 8.57; N, 4.25%). $[\alpha]_D^{20}$ 4.9 (*c* 7 in CH_2Cl_2); ν_{max} (neat liquid) / cm^{-1} 3251 (NH), 2960 (CH), 1447, 1191, 1127 (P=O); δ_H (400 MHz, $CDCl_3$) 0.75 (3H, d, *J* 6.5, MeCH), 0.81 (3H, d, *J* 7.0, MeCH), 0.83 (3H, d, *J* 7.0, MeCH), 0.92 (3H, d, *J* 7.0, MeCH), 1.21-1.38 (2H, m, Me$_2$CHCH$_2$), 1.72-1.85 (1H, m, Me$_2$CH), 1.88-1.97 (1H, m, Me$_2$CH), 2.65-2.75 (1H, m, NH), 2.92-3.05 (1H, m, CH), 7.40-7.48 and 7.89-7.94 (10H, m, ArH); δ_C (100 MHz, $CDCl_3$) 17.52, 17.82, 22.18, 23.26, 24.50, 32.44, 42.63, 54.53, 128.26, 128.39, 128.49, 131.64, 131.77, 132.16, 132.28, 132.36.

(R)-2-Methyl-4-(diphenylphosphinamido)-7-methyloctane (**35**). By following the general procedure described before for the reactions of aziridines with copper catalysed Grignard reagents, aziridine (**6**) (0.90g, 3.0 mmol) was reacted with 2-methylpropyl magnesium bromide (15 mmol, 5 equivalents) and CuBr.SMe_2 (0.012g, 0.06 mmol) in THF for 4 hours to yield (**35**) (0.60g, 60%) as a pale yellow solid. R_f 0.4 [ethyl acetate-hexane (1:1)]; m. p. 115-115.6°C; (Found : C, 73.59; H, 8.98; N, 3.84. $C_{22}H_{32}NPO$ requires C, 73.92; H, 9.02; N, 3.92%). $[\alpha]_D^{20}$ -17.3 (*c* 6 in CH_2Cl_2); ν_{max} (neat liquid) / cm^{-1} 3189 (NH), 2934 (CH), 1436, 1187, 1114 (P=O); δ_H (400 MHz, $CDCl_3$) 0.78 (3H, d, *J* 6.5, MeCH), 0.81 (3H, d, *J* 6.5, MeCH), 0.83 (3H, d, *J* 7.0, MeCH), 0.85 (3H, d, *J* 7.0, MeCH), 1.18-1.55 (7H, m, $Me_2CHCH_2CH_2$ and Me_2CHCH_2), 1.75-1.82 (1H, m, Me_2CH), 2.65-2.79 (1H, m, NH), 3.01-3.17 (1H, m, CH), 7.39-7.46 and 7.89-7.94 (10H, m, ArH); δ_C (100 MHz, $CDCl_3$) 22.58, 22.64, 22.88, 24.70, 28.00, 34.22, 35.16, 46.71 (d, *J* 5.5, CH_2), 49.95 (CH), 128.26, 128.39, 131.58, 132.17, 132.23 (ArC); m / z (CI) 358 (M+1, 85%), 156 (21), 79 (87), 57 (100). Found 358.2286. $C_{22}H_{33}NOP$ requires 358.2230.

General methods for deprotection

Method A: To give free amines. To the *N*-Dpp compound (typically 0.1 mmol) in CH_2Cl_2 (2 ml), under N_2, was added MeOH (2 ml) followed by BF_3OEt_2 (excess). The solution was stirred overnight, after which time H_2O (2 ml) was added. The aqueous layer was then extracted with CH_2Cl_2 (3 x 5ml), basified ($NaHCO_3$) and then extracted with further portions of CH_2Cl_2 (3 x 5ml). These organic layers were then combined, washed with brine (5 ml), dried (Na_2SO_4), filtered and the solvent removed *in vacuo* to yield the free amines in the yields stated.

Method B: To give amine hydrofluoride salts. To the *N*-Dpp compound (typically 0.1 mmol) in CH_2Cl_2 (2 ml), under N_2, was added MeOH (2 ml) followed by BF_3OEt_2 (excess). The solution was then stirred overnight, after which time H_2O (2 ml) was added. The aqueous layer was freeze-dried to produce the hydrofluoride salts of the deprotected compounds.

(R)-3-Amino-4-phenylbutane monohydrofluoride (**36**). By following method B, the *N*-Dpp compound (**9**) (0.07g, 0.2 mmol) was reacted with BF_3OEt_2 (0.2 ml, excess) to yield amine hydrofluoride (**36**) (0.029g, 87%) as a white solid. $[\alpha]_D^{23}$ -5 (*c* 0.4 in MeOH); δ_H (270 MHz, D_2O) 0.98 (3H, t, *J* 7.5, $MeCH_2$), 1.60-1.73 (2H, m, $MeCH_2$), 2.82 (1H, dd, *J* 8.0, 14.0, CH of CH_2Ph), 3.03 (1H, dd, *J* 6.0, 14.0, CH of CH_2Ph), 3.43-3.48 (1H, m, $PhCH_2CH$), 7.28-7.43 (5H, m, ArH); δ_C (67.5 MHz, D_2O) 8.47 (CH_3CH_2), 24.68 ($MeCH_2$), 37.44 (CH_2Ph), 54.21 (CH), 127.15, 128.80, 129.15, 135.73 (ArC); m / z (CI) 172 (M+3, 100), 169 (M, 21) and 102 (89); Found 169.1264. $C_{10}H_{16}NF$ requires 169.1267.

(R)-3-Amino-5-methylhexane monohydrofluoride (**37**). By following method B, the *N*-Dpp compound (**10**) (0.08g, 0.25 mmol) was reacted with BF_3OEt_2 (0.2 ml, excess) to yield amine hydrofluoride (**37**) (0.027g, 80%) as a white solid. (Found : C, 62.41; H, 13.19; N, 10.26. $C_7H_{18}NF$ requires C, 62.22; H, 13.33; N, 10.37%). $[\alpha]_D^{23}$ -6 (*c* 0.3 in MeOH); δ_H (270 MHz, D_2O) 0.80 (6H, 2 x d, *J* 6.5 and 6.5, Me_2CH), 0.84 (3H, t, *J* 7.5, $MeCH_2$), 1.27-1.75 (5H, m, $Me_2CHCH_2CHCH_2Me$), 3.11-3.21 (1H, m, CH); δ_C (67.5 MHz, D_2O) 8.35 ($MeCH_2$), 21.27 and 21.62 (Me_2CH), 23.75 (Me_2CH), 25.27 (CH_2), 40.70 (CH_2), 51.34 (CH); m / z (CI) 116 (M-19, 100) and 114 (31); Found 116.1437. $C_7H_{18}N$ requires 116.1439.

(S)-1-Iodo-2-amino-3-phenylpropane monohydrofluoride ***(38)***. By following method B, the *N*-Dpp compound (**14**) (0.094g, 0.20 mmol) was reacted with BF_3OEt_2 (0.2 ml, excess) to yield amine hydrofluoride (**38**) (0.047g, 84%) as yellow oil. $[\alpha]_D^{23}$ 22 (*c* 0.5 in MeOH); δ_H (270 MHz, D_2O) 2.98 (2H, d, *J* 7.0, $PhC\underline{H}_2$), 3.25 (1H, dd, *J* 5.0, 11.5, C<u>H</u> of $C\underline{H}_2I$), 3.40-3.72 (2H, m, C<u>H</u> of $C\underline{H}_2I$ and C<u>H</u>), 7.27-7.50 (5H, m, Ar<u>H</u>); δ_C (67.5 MHz, D_2O) 38.38 ($\underline{C}H_2$), 52.29 ($\underline{C}H_2$), 52.33 (<u>C</u>H), 127.78, 129.18, 129.43, 134.83 (Ar<u>C</u>); m / z (CI) 265 (M-2, 30%), 264 (M-1, 27), 262 (M-F, 2), 245 (M-NH_3F, 21), 172 (M-95, 100), 171 (75), 136 (39), 135 (20), 118 (24), 117 (94), 92 (21) and 91 (84); Found 262.0096. $C_9H_{13}NI$ requires 262.0093.

(S)-1-Iodo-2-amino-4-methylpentane monohydrofluoride ***(39)***. By following method B, the *N*-Dpp compound (**15**) (0.07g, 0.16 mmol) was reacted with BF_3OEt_2 (0.2 ml, excess) to yield amine hydrofluoride (**39**) (0.032g, 81%) as a clear oil. $[\alpha]_D^{23}$ -5 (*c* 0.4 in MeOH); δ_H (270 MHz, D_2O) 0.90 and 0.92 (6H, 2 x d, *J* 5.5 and 5.5, $\underline{Me}_2CH$), 1.25-1.68 (3H, m, $Me_2C\underline{H}C\underline{H}_2$), 3.26-3.27 (1H, m, $Me_2CHCH_2C\underline{H}$), 3.43 (1H, dd, *J* 5.0, 11.5, C<u>H</u> of $C\underline{H}_2I$), 3.54 (1H, dd, *J* 11.5, 3.5, C<u>H</u> of $C\underline{H}_2I$); m / z (CI) 228 (M-F, 8%), 198 (65) and (185 (100). Found 228.0241. $C_6H_{15}NI$ requires 228.0248.

(S)-1-Phenyl-2-amino-3-thiophenolpropane monohydrofluoride ***(40)***. By following method B, the *N*-Dpp compound (**16**) (0.10g, 0.20 mmol) was reacted with BF_3OEt_2 (3 drops) to yield the amine hydrofluoride (**40**) (0.045g, 85%) as a hygroscopic white solid. $[\alpha]_D^{23}$ -7.2 (*c* 0.4 in MeOH); δ_H (270 MHz, D_2O) 3.03-3.15 (3H, m, $PhC\underline{H}_2$ and C<u>H</u> of $C\underline{H}_2SPh$), 3.34 (1H, dd, *J* 4.0, 15.0, C<u>H</u> of $C\underline{H}_2SPh$), 3.49-3.58 (1H, m, C<u>H</u>), 7.20-7.69 (10H, m, Ar<u>H</u>); δ_C (67.5 MHz, D_2O) 35.24 ($Ph\underline{C}H_2$), 37.43 (<u>C</u>HNH), 52.10 ($\underline{C}H_2SPh$), 124.10, 124.55, 127.56, 129.05, 129.15, 129.31, 129.50, 130.39 (Ar<u>C</u>); m / z (FAB) 244 (M-19, 82%), 233 (86) and 123 (100).

(S)-1-Thiophenol-2-amino-4-methylpentane ***(41)***. By following method A, the *N*-Dpp compound (**17**) (0.09g, 0.22 mmol) was reacted with BF_3OEt_2 (3 drops) to yield amine (**41**) (0.035g, 76%) as a pale yellow oil. (Found : C, 68.54; H, 8.80; N, 6.54. $C_{12}H_{19}NS$ requires C, 68.90; H, 9.09; N, 6.70%). $[\alpha]_D^{23}$ 10.5 (*c* 3 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3301 (NH), 3073 (NH), 2956, 692; δ_H (270 MHz, $CDCl_3$) 0.87 and 0.89 (6H, 2 x d, *J* 6.5 and 6.5, $\underline{Me}_2CHCH_2$), 1.23-1.33 (2H, m, $Me_2CHC\underline{H}_2$), 1.43-1.65 (2H, s, br, $N\underline{H}_2$), 1.67-1.80 (1H, m, $Me_2C\underline{H}CH_2$), 2.72 (1H, dd, *J* 8.5, 13.0, C<u>H</u> of $C\underline{H}_2SPh$), 2.96-3.09 (1H, m, C<u>H</u>), 3.10 (1H, dd, *J* 3.5, 13.0, C<u>H</u> of $C\underline{H}_2SPh$), 7.57-7.38 (5H, m, Ar<u>H</u>); δ_C (67.5 MHz, $CDCl_3$) 22.05 and 23.25 ($\underline{Me}_2CH$), 24.97 ($Me_2\underline{C}H$), 43.14 ($Me_2CH\underline{C}H_2$), 46.49 (<u>C</u>H), 48.13 ($\underline{C}H_2SPh$), 126.10, 128.89, 129.53, 136.30 (Ar<u>C</u>).

(S)-1-Phenyl-2-amino-3-selenophenylpropane monohydrofluoride ***(42)***. By following method B, the *N*-Dpp compound (**18**) (0.10g, 0.20 mmol) was reacted with BF_3OEt_2 (0.20 ml, excess) to yield amine hydrofluoride (**42**) 0.057g, 92%) as a colourless oil. $[\alpha]_D^{23}$ -7.1 (*c* 0.3 in MeOH); δ_H (270 MHz, D_2O) 3.00-3.16 (3H, m, $PhC\underline{H}_2CH$ and C<u>H</u> of $C\underline{H}_2SePh$), 3.30 (1H, dd, *J* 4.5, 14.0, C<u>H</u> of $C\underline{H}_2SePh$), 3.52-3.70 (1H, m, C<u>H</u>), 7.20-7.65 (10H, m, Ar<u>H</u>); δ_C (67.5 MHz, D_2O) 28.64, 38.00 (both $\underline{C}H_2$), 52.80 (<u>C</u>H), 127.53, 128.07, 129.05, 129.28, 129.66, 131.47, 133.15, 135.18 (Ar<u>C</u>); m / z (FAB) 233 (M-Ph, 100%), 133 (27).

(S)-1-Selenophenyl-2-amino-4-methylpentane monohydrofluoride ***(43)***. By following method B, the *N*-Dpp compound (**19**) (0.09g, 0.19 mmol) was reacted with BF_3OEt_2 (0.20 ml, excess) to yield amine hydrofluoride (**43**) (0.046g, 88%) as a pale yellow oil. $[\alpha]_D^{23}$ 11 (*c* 0.4 in MeOH); δ_H (270 MHz, D_2O) 0.70 and 0.90

(6H, 2 x d, *J* 6.5 and 6.5 , $\underline{Me_2}CH$), 1.44-1.84 (3H, m, $Me_2C\underline{H}C\underline{H_2}$), 2.71-3.15 (1H, m, $Me_2CHCH_2C\underline{H}$), 3.42-3.76 (2H, m, $PhSeC\underline{H_2}$), 7.32-7.74 (5H, m, Ar$\underline{H}$); m / z (CI) 261 (25), 260 (24), 259 (39), 258 (M-F, 28), 257 (24), 256 (16), 241 (98), 239 (50), 173 (100), 172 (60), 171 (58), 170 (43), 169 (43), 168 (18) and 102 (52); Found 258.0743. $C_{12}\ _{20}NSe$ requires 258.0761.

(S)-1-Cyano-2-amino-3-phenylpropane (**44**). By following method A, the Dpp protected compound (**21**) (0.04g, 0.11 mmol) was reacted with BF_3OEt_2 (3 drops) to yield amine (**44**) (0.016g, 89%) as a clear oil. $[\alpha]_D^{23}$ -9.4 (*c* 1 in CH_2Cl_2); δ_H (270 MHz, $CDCl_3$) 2.37 (1H, dd, *J* 6.5, 16.5, C$\underline{H}$ of $C\underline{H_2}Ph$), 2.49 (1H, dd, *J* 16.5, 5.0, C$\underline{H}$ of $C\underline{H_2}Ph$), 2.75 (1H, dd, *J* 7.5, 13.5, C$\underline{H}$ of $C\underline{H_2}CN$), 2.85 (1H, dd, *J* 6.0, 13.5, C$\underline{H}$ of $C\underline{H_2}CN$), 3.33-3.43 (1H, m, $PhCH_2C\underline{H}$), 7.17-7.37 (5H, m, Ar$\underline{H}$); m / z (CI) 120 (M-CH_2CN, 84%), 91 (75), 84 (100) and 51 (88); Found 120.0811. $C_8H_{10}N$ requires 120.0813.

(S)-2-Methyl-4-amino-5-cyanopentane mono hydrofluoride (**45**). By following method B, the *N*-Dpp compound (**22**) (0.07g, 0.16 mmol) was reacted with BF_3OEt_2 (3 drops) to yield amine hydrofluoride (**45**) (0.021g, 89%) as a hygroscopic white solid. $[\alpha]_D^{23}$ -5 (*c* 0.5 in MeOH); δ_H (270 MHz, D_2O) 0.96 (3H, d, *J* 5.5, $\underline{Me}CH$), 0.98 (3H, d, *J* 5.0, $\underline{Me}CH$), 1.66-1.80 (3H, m, $Me_2C\underline{H}C\underline{H_2}$), 3.01 (2H, d, *J* 5.0, $C\underline{H_2}CN$), 3.68-3.80 (1H, m, C$\underline{H}$); δ_C (67.5 MHz, D_2O) 21.11, 21.33, 23.68 ($\underline{Me_2}CH$), 40.54, 46.10 ($\underline{C}H_2$), 116.99 ($\underline{C}N$); m / z (CI) 128 (9%), 127 (M-F, 5) and 87 (100).

(R)-1-Phenyl-2-aminopentane monohydrofluoride (**46**). By following method B, the *N*-Dpp compound (**23**) (0.09g, 0.19 mmol) was reacted with BF_3OEt_2 (0.1 ml, excess) to yield amine hydrofluoride (**46**) (0.025g, 73%) as a white solid. $[\alpha]_D^{23}$ 11 (*c* 0.2 in MeOH); δ_H (270 MHz, D_2O) 0.80 (3H, t, *J* 7.5, $\underline{Me}CH_2$), 1.25-1.40 (2H, m, $C\underline{H_2}$), 1.43-1.57 (2H, m, $C\underline{H_2}$), 2.74 (1H, dd, *J* 8.0, 14.5, C$\underline{H}$ of $C\underline{H_2}Ph$), 2.94 (1H, dd, *J* 6.5, 14.5, C$\underline{H}$ of $C\underline{H_2}Ph$), 3.38-3.68 (1H, m, C$\underline{H}$), 7.18-7.48 (5H, m, Ar$\underline{H}$); δ_C (67.5 MHz, D_2O) 12.83 (Me), 17.84 ($\underline{C}H_2$), 33.84 ($\underline{C}H_2$), 38.07 ($\underline{C}H_2$), 52.89 ($\underline{C}H$), 127.37, 128.99, 129.40, 135.98 (Ar$\underline{C}$); m / z (CI) 164 (M-19, 21%), 147 (35), 119 (19), 105 (12), 91 (86) and 72 (100). Found 164.1437. $C_{11}H_{18}N$ requires 164.1439.

(R)-2-Methyl-4-aminoheptane monohydrofluoride (**47**). By following method B, the *N*-Dpp compound (**24**) (0.08g, 0.24 mmol) was reacted with BF_3OEt_2 (0.2 ml, excess) to yield amine hydrofluoride (**47**) (0.027g, 76%) as a white solid. $[\alpha]_D^{23}$ -5.5 (*c* 1.3 in MeOH); δ_H (270 MHz, D_2O) 0.98 (6H, 2 x d, *J* 6.5 and 6.5, $\underline{Me_2}CH$), 0.99 (3H, t, *J* 5.5, $\underline{Me}CH_2$), 1.25-1.70 (7H, m, $Me_2C\underline{H}C\underline{H_2}CHC\underline{H_2}C\underline{H_2}CH_3$), 3.30-3.41 (1H, m, $Me_2CHCH_2C\underline{H}$); δ_C (67.5 MHz, D_2O) 12.89 ($\underline{Me}CH_2$), 17.56 ($Me\underline{C}H_2$), 21.37, 21.56 ($\underline{Me_2}CH$), 23.72 ($Me_2\underline{C}H$), 34.32 ($\underline{C}H_2$), 41.15 ($\underline{C}H_2$), 49.84 ($Me_2CHCH_2\underline{C}H$); m / z (CI) 130 (M-19, 10%), 86 (95) and 72 (100). Found 130.1589. $C_8H_{20}N$ requires 130.1596.

(R)-2-Methyl-4-amino-5-phenylpentane monohydrofluoride (**48**). By following method B, the *N*-Dpp compound (**25**) (0.10g, 0.26 mmol) was reacted with BF_3OEt_2 (0.1 ml, excess) to yield amine hydrofluoride (**48**) (0.042g, 82%) as a white solid. $[\alpha]_D^{23}$ 7.2 (*c* 0.5 in MeOH); δ_H (270 MHz, D_2O) 0.80 and 0.84 (6H, 2 x d, *J* 6.4 and 6.4, $\underline{Me_2}CH$), 1.41-1.46 (2H, m, $Me_2CHC\underline{H_2}$), 1.60-1.70 (1H, m, $Me_2C\underline{H}$), 2.78 (1H, dd, *J* 7.5, 14.0, C$\underline{H}$ of $C\underline{H_2}Ph$), 2.98 (1H, dd, *J* 6.0, 14.2, C$\underline{H}$ of $C\underline{H_2}Ph$), 3.51-3.72 (1H, m, $PhCH_2C\underline{H}$), 7.22-7.37 (5H,

m, ArH); δ_C (67.5 MHz, D_2O) 21.14 and 21.56 (Me_2CH), 23.72 (Me_2CH), 38.45 (Me_2CHCH_2), 40.96 ($PhCH_2$), 51.27 (CH), 127.37, 128.96, 129.43, 135.82 (ArC); m / z (CI) 178 (M-19, 37%), 176 (26), 161 (M-NH_3^+, 20), 120 (100), 119 (72) and 105 (81); Found 178.1598. $C_{12}H_{20}N$ requires 178.1596. The opposite enantiomer, (**53**) was produced in 89% from *N*-Dpp compound (**30**) following an identical procedure.

2-Methyl-4-amino-6-methylheptane monohydrofluoride (***49***). By following method B, the *N*-Dpp compound (**26**) (0.086g, 0.25 mmol) was reacted with BF_3OEt_2 (0.2 ml, excess) to yield amine hydrofluoride (**49**) (0.031g, 77%) as a white solid. (Found : C, 66.42; H, 13 61; N, 8. 23. $C_9H_{22}NF$ requires C, 66.26; H, 13.50; N 8.59%). $[\alpha]_D^{23}$ 0 (*c* 2 in MeOH); δ_H (270 MHz, D_2O) 0.81 and 0.82 (12H, 2 x d, *J* 6.5 and 6.5, Me_2CH), 1.28-1.41 (4H, m, Me_2CHCH_2), 1.44-1.65 (2H, m, Me_2CH), 3.21-3.28 (1H, m, Me_2CHCH_2CH); δ_C (67.5 MHz, D_2O) 21.18 and 21.68 (Me_2CH), 23.68 (Me_2CH), 41.72 (Me_2CHCH_2), 48.38 (Me_2CHCH_2CH); m / z (CI) 144 (M-F, 66%), 143 (36), 142 (100) and 128 (37); Found 144.1748. $C_9H_{22}N$ requires 144.1752.

(R)-1-Phenyl-2-aminoheptane monohydrofluoride (***50***). By following method B, the *N*-Dpp compound (**27**) (0.10g, 0.27 mmol) was reacted with BF_3OEt_2 (0.1 ml, excess) to yield amine hydrofluoride (**50**) (0.045g, 79%) as a white solid. $[\alpha]_D^{23}$ 11 (*c* 0.4 in MeOH); δ_H (270 MHz, D_2O) 0.77 (3H, t, *J* 7.5, $MeCH_2$), 1.04-1.55 (8H, m, $MeCH_2CH_2CH_2CH_2$), 2.78 (1H, dd, *J* 8.0, 14.5, CH of CH_2Ph), 2.97 (1H, dd, *J* 14.5, 6.0, CH of CH_2Ph), 3.42-3.47 (1H, m, $PhCH_2CH$), 7.11-7.33 (5H, m, ArH); δ_C (67.5 MHz, D_2O) 13.11 ($MeCH_2$), 21.59, 23.94, 30.54, 31.62 (CH_2), 38.00 ($PhCH_2$), 53.08 (CH), 127.34, 128.96, 129.37, 135.98 (ArC); m / z (CI) 192 (M-F, 9%), 175 (M-NH_3F, 7), 122 (13), 121 (17), 119 (25), 105 (22) and 102 (100); Found 192.1755. $C_{13}H_{22}N$ requires 192.1752.

(R)-2-Methyl-4-aminononane monohydrofluoride (***51***). By following method B, the *N*-Dpp compound (**28**) (0.08g, 0.22 mmol) was reacted with BF_3OEt_2 (0.2 ml, excess) to yield amine hydrofluoride (**51**) (0.031g, 80%) as a hygroscopic solid. $[\alpha]_D^{23}$ 3.9 (*c* 0.2 in MeOH); δ_H (270 MHz, D_2O) 1.40 (6H, d, *J* 6.5 and 6.5, Me_2CH), 1.55 (3H, t, *J* 5.5, $MeCH_2$), 1.20-1.80 (11H, m, $Me_2CHCH_2CHCH_2CH_2CH_2CH_2CH_3$), 3.01-3.21 (1H, m, Me_2CHCH_2CH); δ_C (67.5 MHz, D_2O) 8.19 ($MeCH_2$), 13.14 (Me_2CH), 21.33 and 21.65 (Me_2CH), 23.75, 30.67, 32.19, 41.21, 46.67 (CH_2), 50.16 (Me_2CHCH_2CH); m / z (CI) 161 (M+3-F, 59%), 158 (M-F, 9), 103 (100) and 102 (82); Found 158.1903. $C_{10}H_{24}N$ requires 158.1909.

1-Phenyl-2-amino-3-phenylpropane monohydrofluoride (***52***). By following method B, the *N*-Dpp compound (**29**) (0.09g, 0.22 mmol) was reacted with BF_3OEt_2 (0.2 ml, excess) to yield amine hydrofluoride (**52**) (0.046g, 91%) as a clear oil. $[\alpha]_D^{23}$ 0 (*c* 0.7 in MeOH); δ_H (270 MHz, D_2O) 2.82 (2H, dd, *J* 5.5, 13.0, CH of CH_2Ph), 3.01 (2H, dd, *J* 13.5, 6.0, CH of CH_2Ph), 3.60-3.72 (1H, m, $PhCH_2CH$), 7.20-7.80 (10H, m, ArH); δ_C (67.5 MHz, D_2O) 38.10, 54.19, 127.47, 128.83, 129.37, 135.63; m / z (CI) 212 (M-19, 13%), 120 (100), 91 (36). Found 212.1435. $C_{15}H_{18}N$ requires 212.1439.

(R)-1-Cyclopentyl-2-amino-3-phenylpropane monohydrofluoride (***54***). By following method B, the *N*-Dpp compound (**31**) (0.07g, 0.17 mmol) was reacted with BF_3OEt_2 (0.2 ml, excess) to yield amine hydrofluoride (**54**) (0.026g, 68%) as a white solid. $[\alpha]_D^{23}$ 5 (*c* 0.3 in MeOH); δ_H (270 MHz, D_2O) 1.02-2.08 (11H, m,

cyclopentyl and CH_2cyclopentyl), 3.00 (1H, dd, *J* 8.0, 14.2, CH of $PhCH_2$), 3.19 (1H, dd, *J* 6.2, 14.2, CH of $PhCH_2$), 3.62-3.72 (1H, m, $PhCH_2CH$), 7.42-7.57 (5H, m, ArH); δ_C (67.5 MHz, D_2O) 24.41, 31.81, 32.00 (CH_2), 35.49 (CH), 38.22, 38.45 (CH_2), 52.61 (CH), 127.40, 129.02, 129.47, 136.02 (ArC); m / z (CI) 204 (M-19, 27%), 187 (9), 120 (15) and 112 (100); Found 204.1744. $C_{14}H_{22}N$ requires 204.1752.

(S)-1-Cyclopentyl-2-amino-4-methylpentane monohydrofluoride (**55**). By following method B, the *N*-Dpp compound (**32**) (0.10g, 0.26 mmol) was reacted with BF_3OEt_2 (0.1 ml, excess) to yield amine hydrofluoride (**55**) (0.042g, 85%) as a white solid. (Found : C, 70.02; H, 12.82; N, 7.15. $C_{11}H_{24}NF$ requires C, 69.84; H, 12.70; N, 7.41%). $[\alpha]_D^{23}$ -5.2 (*c* 0.5 in MeOH); δ_H (270 MHz, D_2O) 0.85 (6H, 2 x d, *J* 6.5 and 6.5, Me_2CH), 0.89-1.08 and 1.20-1.85 (14H, m, $Me_2CHCH_2CHCH_2$Cyclopentyl), 3.19-3.27 (1H, m, Me_2CHCH_2CH); δ_C (67.5 MHz, D_2O) 21.24 and 21.72 (Me_2CH), 23.78 (Me_2CH), 24.45, 31.87, 32.13 (CH_2), 35.49 (CH), 38.89, 41.69 (CH_2), 49.72 (Me_2CHCH_2CH); m / z (FAB) 170 (M-F, 100).

(R)-2-Methyl-3-amino-6-methylheptane (**56**). By following method A the *N*-Dpp amine (**33**) (0.80g, 2.3 mmol) was treated with BF_3OEt_2 (7.00 ml, 10 equivalents) to yield amine (**56**). R_f 0.1 (ethyl acetate); δ_H (400 MHz, $CDCl_3$) 0.85 (3H, d, *J* 6.8, MeCH), 0.86 (3H, d, *J* 6.8, MeCH), 0.88 (3H, d, *J* 6.8, MeCH), 0.89 (3H, d, *J* 6.8, MeCH), 1.24-1.86 (8H, m, $Me_2CHCH_2CH_2$ and Me_2CH and NH_2), 3.21-3.29 (1H, m, CH).

(R)-2-Methyl-3-amino-5-methylhexane (**57**). By following method A the *N*-Dpp amine (**34**) (0.37g, 1.0 mmol) was treated with BF_3OEt_2 (1.37 ml, 10 equivalents) to yield amine (**57**). R_f 0.1 (ethyl acetate); δ_H (400 MHz, $CDCl_3$) 0.92 (3H, d, *J* 6.8, MeCH), 0.94 (3H, d, *J* 6.8, MeCH), 0.98 (3H, d, *J* 6.8, MeCH), 1.01 (3H, d, *J* 6.8, MeCH), 1.16-1.79 (7H, m, Me_2CHCH_2 and Me_2CH and NH_2), 3.18-3.22 (1H, m, CH).

(R)-2-Methyl-4-amino-7-methyl octane (**58**). By following method A the *N*-Dpp amine (**35**) (0.60g, 1.7 mmol) was treated with BF_3OEt_2 (2.9 ml, 10 equivalents) to yield amine (**58**). R_f 0.1 (ethyl acetate); δ_H (400 MHz, $CDCl_3$) 0.88 (6H, d, *J* 6.8, 2MeCH), 0.89 (6H, d, *J* 7.2, 2MeCH), 1.14-1.56 (8H, m, $Me_2CHCH_2CH_2$ and Me_2CHCH_2), 1.67-1.75 (1H, m, CH), 2.62-2.81 (2H, s, br, NH_2).

(S)-1-(O-Diphenylphosphinyl)-2-(p-toluenesulphonamido)-3-phenylpropane (**59**). R_f 0.26 [ethyl acetate-light petroleum (1:1)]; m.p. 140 °C; (Found : C, 66.18; H 5.87; N, 2.68; S, 6.06; P 6.59. $C_{28}H_{28}NPO_4S$ requires C, 66.52; H, 5.58; N, 2.77; S, 6.34; P, 6.13%). $[\alpha]_D^{23}$ 5.3 (*c* 9 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3100 (NH), 2880 (CH), 1610, 1480, 1360, 1220, 1170, 1030 (S=O and P=O), 960, 620; δ_H (270 MHz, $CDCl_3$) 2.32 (3H, s, CCH_3), 2.87 (1H, dd, *J* 8.5, 13.5, CH of $PhCH_2$), 2.95 (1H, dd, *J* 6.0, 13.5 Hz, CH of CH_2Ph), 3.59-3.60 (1H, m, CH), 3.81-3.93 (2H, m, CH_2OPOPh_2), 6.22 (1H, d, *J* 6.0, NH), 7.19-7.83 (19H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 21.43 (CCH_3), 38.40 ($PhCH_2$), 55.05 (d, *J* 4.3, CH), 66.01 (d, *J* 6.5, CH_2OPOPh_2), 126.69, 127.00, 128.61, 128.75, 128.81, 129.27, 129.46, 131.46, 131.62, 131.65, 131.81, 132.51, 136.81, 137.61, 142.88 (ArC); δ_P (161.7 MHz, $CDCl_3$) 34.51; m / z (EI) 414 (M-91, 42%), 196 (71), 132 (48), 105 (28) and 91 (100).

(S)-1-(O-Diphenylphosphinyl)-2-(p-toluenesulphonamido)-4-methylpentane (**60**). R_f 0.33 [ethyl acetate-light petroleum (1:1)]; m.p. 164-165 °C; (Found : C, 63.50; H, 6.43; N, 2.93; S, 6.71; P, 6.51. $C_{25}H_{30}NPSO_4$

requires C, 63.68; H, 6.41; N, 2.97; S, 6.80; P, 6.57%). $[\alpha]_D^{23}$ 8 (c 20 in CH_2Cl_2); ν_{max} (CCl_4) / cm^{-1} 3080 (NH), 2980 (CH), 1450, 1220, 1140 (S=O and P=O); δ_H (270 MHz, $CDCl_3$) 0.74 and 0.80 (6H, 2 x d, *J* 6.5, $\underline{Me}_2CH$), 1.24-1.65 (3H, m, $Me_2C\underline{H}C\underline{H}_2$), 2.33 (3H, s, $CC\underline{H}_3$), 3.43-3.52 (1H, m, $Me_2CHCH_2C\underline{H}$), 3.83 (1H, dd, *J* 4.0, 10.5, C<u>H</u> of $C\underline{H}_2ODpp$), 3.91 (1H, dd, *J* 10.5, 4.0, C<u>H</u> of $C\underline{H}_2ODpp$), 6.21 (1H, d, *J* 5.0, N<u>H</u>), 7.10 (2H, d, *J* 8.0, 2 Tosyl Ar<u>H</u>), 7.38-7.97 (12H, m, Ar<u>H</u>); δ_C (67.5 MHz, $CDCl_3$) 21.32, 21.92, 22.55 (<u>Me</u>), 24.08 (<u>C</u>H), 41.14 ($\underline{C}H_2$), 51.75 (d, *J* 5.4, CH), 67.08 (d, *J* 6.5, $\underline{C}H_2$), 126.86, 128.38, 128.59, 129.34, 131.33, 131.50, 131.54, 131.65, 131.69, 132.24, 138.15, 142.77 (ArC); δ_P (161.7 MHz, $CDCl_3$) 33.54; m / z (EI) 471 (M^+, 10%), 414 (M-57, 5), 231 (100), 219 (79), 201 (47), 91 (65), 77 (19) and 42 (20); Found 471.1633. $C_{25}H_{30}NO_4PS$ requires 471.1626.

'One pot' Synthesis of aziridines

To a solution of the respective β-aminoalcohol (typically 1.5 mmol) in THF, under N_2, at 0°C, was added DppCl (2 equivalents) and Et_3N (3 equivalents). A white precipitate of triethylamine hydrochloride was immediately formed. The suspension was stirred at 0°C to room temperature for 20 hours, afterwhich time it was recooled to 0°C and NaH (10 equivalents) added. The suspension was stirred at 0°C to room temperature for a further 20 hours and then H_2O (one equivalent based on NaH) was added. The solution was then filtered through anhydrous magnesium sulfate and the resulting filter cake washed with ether (100 ml). The solvent was then removed *in vacuo* to leave a gum which was purified by column chromatography on silica gel with ethyl acetate as eluent.

(S)-N-Diphenylphosphinyl-2-benzyl aziridine (***5***). By following the general procedure described above (2*S*)-(-)-2-amino-3-phenylpropanol (0.2 g, 1.3 mmol), DppCl (0.51 ml, 2.6 mmol), Et_3N (0.55 ml, 4.0 mmol) and NaH (0.4g, 16.6 mmol) in THF (20 ml) were reacted to yield aziridine (**5**) (0.38 g, 86%) as a white solid. The data obtained for this solid was exactly analogous to that reported previously.

(S)-N-Diphenylphosphinyl-2-(2-methylpropyl) aziridine (***6***). By following the general procedure described above (2*S*)-leucinol (0.2 g, 1.7 mmol), DppCl (0.65 ml, 3.4 mmol), Et_3N (0.71 ml, 5.1 mmol) and NaH (0.4g, 16.6 mmol) in THF (20 ml) were reacted to yield aziridine (**6**) (0.40 g, 78%) as a white solid. The data obtained for this solid was exactly analogous to that reported previously.

(S)-N-Diphenylphosphinyl-2-(2-methyl)ethyl aziridine (***61***). By following the general procedure described above (2*S*)-(+)-amino-3-methylbutanol (0.2 g, 1.9 mmol), DppCl (0.75 ml, 3.8 mmol), Et_3N (0.81 ml, 5.8 mmol) and NaH (0.4g, 16.6 mmol) in THF (20 ml) were reacted to yield aziridine (**61**) (0.37g, 67%) as a clear oil. R_f 0.25 (ethyl acetate); $[\alpha]_D^{20}$ -14.9 (c 1 in CH_2Cl_2); (Found : C, 71.1; H, 7.2; N, 5.2. $C_{17}H_{20}NOP$ requires C, 71.5; H, 7.1; N, 4.9%). ν_{max} (neat liquid) / cm^{-1} 3060, 2920 (CH), 1440, 1200, 1189, 1129 (P=O), 740 (aromatic); δ_H (400 MHz, $CDCl_3$) 0.70 and 0.88 (6H, 2 x d, *J* 6.5, $\underline{Me}_2CH$), 1.40-1.52 (1H, m, $Me_2C\underline{H}$), 1.92 (1H, ddd, *J* 1.0, 3.5, 12.5, C<u>H</u> of $C\underline{H}_2NH$), 2.41 (1H, ddd, *J* 1.0, 6.0, 17.5, C<u>H</u> of $C\underline{H}_2NH$), 2.44-2.61 (1H, m, $Me_2CHC\underline{H}$), 7.41-7.47 and 7.90-7.96 (10H, m, Ar<u>H</u>); δ_C (100 MHz, $CDCl_3$) 19.10, 19.74 (both $\underline{Me}_2CH$), 28.20 (d, *J* 7.5, $Me_2\underline{C}$), 30.76 (d, *J* 4.0, <u>C</u>H)), 41.60 (d, *J* 6.0, $\underline{C}H_2$), 128.16, 128.28, 128.38, 128.50, 130.34, 131.58, 131.67, 131.74, 131.78, 131.87, 132.36 (ArC); m / z (CI) 286 (M+1, 100%), 208 (28) and 79 (36); Found 286.1336. $C_{17}H_{21}NOP$ requires 286.1361.

(S)-N-Diphenylphosphinyl-2-phenyl aziridine (**62**). By following the general procedure described above (2*S*)-(+)-2-amino-2-phenylethanol (0.2 g, 1.5 mmol), DppCl (0.56 ml, 2.9 mmol), Et_3N (0.61 ml, 4.4 mmol) and NaH (0.4g, 16.6 mmol) in THF (20 ml) were reacted to yield a yellow oil. Crystallisation from chloroform / hexane afforded aziridine (**62**) (0.24g, 52%) as a colourless solid. R_f 0.3 (ethyl acetate); m.p. 91 °C; $[\alpha]_D^{23}$ -4.6 (*c* 5 in CH_2Cl_2); (Found : C, 75.00; H, 5.85; N, 4.35. $C_{20}H_{18}NOP$ requires C, 75.2; H, 5.7; N, 4.4%); ν_{max} ($CHCl_3$) / cm^{-1} 3061 (CH), 1591, 1581, 1258, 1125 (P=O), 1011, 842, 728 (aromatic); δ_H (270 MHz, $CDCl_3$) 2.19 (1H, ddd, *J* 1.5, 3.0, 13.0, C<u>H</u> of C<u>H</u>$_2$N), 2.86 (1H, ddd, *J* 1.5, 6.0, 18.0, C<u>H</u> of C<u>H</u>$_2$N), 3.74 (1H, ddd, *J* 3.0, 6.0, 15.5, C<u>H</u>N), 7.25-7.50 and 7.83-8.01 (15H, m, Ar<u>H</u>); δ_C (67.5 MHz, $CDCl_3$) 32.97 (d, *J* 7.0, <u>C</u>H$_2$), 36.81 (d, *J* 7.0, <u>C</u>H), 126.2-137.6 (Ar<u>C</u>); δ_P (121.4 MHz, $CDCl_3$) 32.67; m / z (CI) 320 (MH^+, 100%), 242 (27), 201 (Ph_2PO, 36), 118 (60); Found 320.1194. $C_{21}H_{18}NOP$ requires 320.1204.

(S)-N-Diphenylphosphinyl-2-methyl aziridine (**63**). By following the general procedure described above (2*S*)-(+)-2-aminopropanol (0.2 g, 2.7 mmol), DppCl (1.0 ml, 5.3 mmol), Et_3N (1.12 ml, 8.0 mmol) and NaH (0.5g, 20.8 mmol) in THF (20 ml) were reacted to yield a colourless oil. Crystallisation from ethyl acetate / hexane afforded aziridine (**63**) (0.38 g, 56%) as a colourless solid. R_f 0.25 (ethyl acetate); m.p. 119.5-120.5 °C; $[\alpha]_D^{23}$ -3.7 (*c* 1 in CH_2Cl_2); (Found : C, 70.15; H, 6.40; N, 5.35. $C_{15}H_{16}NOP$ requires C, 70.0; H, 6.3; N, 5.45%). ν_{max} (CCl_4) / cm^{-1} 3060, 2928 (CH), 1438, 1399, 1249, 1203, 1126 (P=O), 1111, 996, 695 (aromatic); δ_H (270 MHz, $CDCl_3$) 1.27 (3H, d, *J* 5.5, C<u>H</u>$_3$), 1.88 (1H, ddd, *J* 1.0, 3.5, 12.5, C<u>H</u> of C<u>H</u>$_2$N), 2.47 (1H, ddd, *J* 1.0, 6.0, 17.5, C<u>H</u> of C<u>H</u>$_2$N), 2.52-2.59 (1H, m, CH_3C<u>H</u>N), 7.41-7.52 (6H, m, Ar<u>H</u>), 7.90-7.98 (4H, m, Ar<u>H</u>); δ_C (67.5 MHz, $CDCl_3$) 17.38 (d, *J* 4.5, <u>C</u>H$_3$), 29.69 (d, *J* 6.0, <u>C</u>H$_2$), 30.58 (d, *J* 6.0, <u>C</u>H), 127.84-132.84 (Ar<u>C</u>); δ_P (121.4 MHz, $CDCl_3$) 32.02; m / z (CI) 258 (MH^+, 100%), 215 (24), 201 (Ph_2PO, 60), 180 (35), 56 (47). Found 258.1048. $C_{16}H_{16}NOP$ requires 258.1048.

(S)-N-Diphenylphosphinyl-2-(2-methylthioethyl) aziridine (**64**). By following the general procedure described above (2*S*)-(-)-2-amino-4-methylthiobutanol (0.1 ml, 1.1 mmol), DppCl (0.43 ml, 2.2 mmol), Et_3N (0.47 ml, 3.4 mmol) and NaH (0.4g, 16.6 mmol) in THF (20 ml) were reacted to yield aziridine (**64**) (0.28 g, 79%) as a clear oil. R_f 0.2 (ethyl acetate); $[\alpha]_D^{23}$ -10.3 (*c* 5 in CH_2Cl_2); (Found : C, 64.4; H, 6.60; N, 4.35. $C_{17}H_{20}NOPS$ requires C, 64.3; H, 6.35; N, 4.4%); ν_{max} (CCl_4) / cm^{-1} 2913 (CH), 1742, 1480, 1127 (P=O), 960, 729, 696 (aromatic); δ_H (400 MHz, CDCl3) 1.66-1.74 and 1.82-1.91 (2H, 2 x m, CH_2C<u>H</u>$_2$CH), 1.98 (3H, s, <u>Me</u>S), 2.01 (1H, dd, *J* 3.0, 12.5, C<u>H</u> of C<u>H</u>$_2$N), 2.22-2.35 (2H, m, CH_3SC<u>H</u>$_2$), 2.57 (1H, dd, *J* 3.0, 12.5, C<u>H</u> of C<u>H</u>$_2$N), 2.76-2.81 (1H, m, C<u>H</u>N), 7.28-7.53 (6H, m, Ar<u>H</u>), 7.78-7.95 (4H, m, Ar<u>H</u>); δ_C (67.5 MHz, $CDCl_3$) 15.46 (S<u>C</u>H$_3$), 29.48 (d, *J* 7.0, <u>C</u>H$_2$CHN), 31.37 (CH_3S<u>C</u>H$_2$), 32.32 (d, *J* 4.0, CH<u>C</u>H$_2$N), 34.47 (d, *J* 6.0, <u>C</u>HN), 128.39-132.7 (Ar<u>C</u>); δ_P (161.9 MHz, $CDCl_3$) 31.78; m / z (CI) 318 (MH^+, 97%), 304 (M-Me, 21), 270 (M-MeS, 59), 218 (60), 210 (Ph_2PO, 100), 61 (88). Found 318.1080. $C_{18}H_{20}NOPS$ requires 318.1082.

(S)-N-Diphenylphosphinyl-2-(1-methylpropyl) aziridine (**65**). By following the general procedure described above (*S*)-(+)-isoleucinol (0.2 g, 1.7 mmol), DppCl (0.65 ml, 3.4 mmol), Et_3N (0.71 ml, 5.1 mmol) and NaH (0.4g, 16.6 mmol) in THF (20 ml) were reacted to yield aziridine (**65**) (0.45 g, 87%) as a pale yellow oil. R_f 0.25 (ethyl acetate); $[\alpha]_D^{23}$ -15.0 (*c* 5 in CH_2Cl_2); (Found : C, 72.1; H, 7.5; N, 4.7. $C_{18}H_{22}NOP$ requires C, 72.2; H, 7.4; N, 4.7%); ν_{max} (CCl_4) / cm^{-1} 2928 (CH), 1572, 1126 (P=O), 944, 692 (aromatic); δ_H (400 MHz, $CDCl_3$) 0.67 (3H, t, *J* 7.5, CH_2C<u>H</u>$_3$), 0.86 (3H, d, *J* 7.0, CHC<u>H</u>$_3$), 0.95 (1H, m,

$CH_3CH_2CH(CH_3)$), 1.18-1.32 (2H, m, $CH_3CH_2CH(CH_3)$), 1.93 (1H, ddd, *J* 1.0, 3.5, 12.5, CH of CH_2N), 2.46 (1H, ddd, *J* 1.0, 6.0, 18.0, CH of CH_2N), 2.55-2.63 (1H, m, CHN), 7.39-7.51 (6H, m, ArH), 7.87-7.95 (4H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 10.44 (CH_2CH_3), 15.05 ($CH(CH_3)CH$), 26.80 (CH_3CH_2), 27.33 (d, *J* 13.0, $CHCH_2N$), 36.49 ($CH(CH_3)$), 40.16 (d, *J* 4.0, CHN), 128.29-132.79 (ArC); δ_P (161.9 MHz, $CDCl_3$) 31.83; m / z (CI) 300 (MH^+, 100%), 222 (41), 201 (Ph_2PO, 55), 98 (65). Found 300.1520. $C_{18}H_{23}NOP$ requires 300.1517.

N,O-bis-(Diphenylphosphinyl)-2-(hydroxymethyl) aziridine (**66**). By following the general procedure described above 2-amino-1,3-propanediol (0.5 g, 5.5 mmol), DppCl (3.2 ml, 16.5 mmol), Et_3N (3.1 ml, 22.0 mmol) and NaH (1.0 g, 41.7 mmol) in THF (100 ml) were reacted to yield a colourless oil. Crystallisation from EtOAc / hexane gave aziridine (**66**) (1.56 g, 60%) as a white solid. R_f 0.4 (10% methanol, ethyl acetate); m.p. 138-139°C; (Found : C, 68.3; H, 5.4; N, 2.8. $C_{27}H_{25}NO_3P_2$ requires C, 68.5; H, 5.3; N, 3.0%); ν_{max} ($CHCl_3$) / cm^{-1} 2982 (CH), 1438, 1132 (P=O), 1022, 834 (aromatic); δ_H (300 MHz, $CDCl_3$) 2.03 (1H, dd, *J* 3.0, 12.5, CH of CH_2N), 2.58 (1H, dd, *J* 6.0, 16.0, CH of CH_2N), 3.04-3.19 (1H, m, CHN), 3.89-3.97 and 4.19-4.23 (2H, 2 x m, CH_2ODpp), 7.27-7.95 (20H, m, ArH); δ_C (67.5 MHz, $CDCl_3$) 26.85 (CH_2N), 34.13 (CHN), 65.69 (CH_2ODpp), 128.8-131.5 (ArC); δ_P (161.9 MHz, $CDCl_3$) 31.91 and 32.68; m / z (CI) 474 (MH^+, 95%), 419 (9), 274 (M-Ph_2PO, 9), 219 (100), 201 (Ph_2PO, 41). Found 474.1376. $C_{27}H_{26}NO_3P_2$ requires 474.1387.

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