Synthesis and applications to asymmetric catalysis of a series of mono- and bis(diazaphospholidine) ligands

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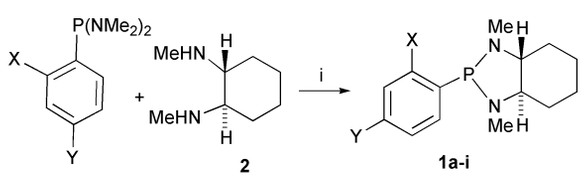
The synthesis of a series of closely related mono- and bis(diazaphospholidine) ligands has been achieved using the condensation of a diamine with a bis(dimethylamino)arylphosphine. The resulting ligands have given excellent results in palladium-catalysed allylic substitution reactions to form C–C bonds (up to 89% ee) and C–N bonds (up to 78% ee).

Introduction

Asymmetric catalysis continues to be an area of major worldwide research effort.[1] Allylic substitution reactions in particular have benefited from the introduction of several excellent ligands.[2] Of these, diphosphines and combined phosphine–amine donors have proven to be especially well suited to the required role.[2] As part of an ongoing programme[3] directed at the development of a range of phosphorus donor ligands with a wide range of applications to asymmetric synthesis, we have investigated diazaphospholidines **1** in this capacity. We anticipated that such ligands would benefit from a high level of conformational rigidity and would provide a suitable chiral environment within organometallic complexes. Furthermore, we were aware of the facile synthesis of such materials from the corresponding C_2-symmetric chiral diamines.[4,5]

Results and discussion

The preparation of a series of ligands was achieved following literature precedents (Scheme 1).[4] The bis(dimethylamino)-



Compound	X	Y	Yield
1a	H	H	100%
1b	H	OMe	96%
1c	OCH_3	H	100%
1d	SCH_3	H	98%
1e	CH_2CH_3	H	96%
1f	$CH(CH_3)_2$	H	100%
1g	Br	H	97%
1h	CH_2OCH_3	H	91%
1i	see structure	H	100%

Scheme 1 *Reagents and conditions*: i) PhMe, heat 8–12 h.

phosphine precursors to **1a**–**c**, **1e**, **1h** and **1i** were formed by the reaction of the corresponding lithiated aromatic compound with preformed $(Me_2N)_2PCl$. The corresponding precursors for **1d** and **1f** could not be prepared by this method. However, lithiation and transmetallation with zinc dichloride, followed by reaction with phosphorus trichloride and subsequent treatment with an excess of dimethylamine proved successful. The precursor to compound **1g** was synthesised following the published procedure of Drewelies and Latscha.[6] Each intermediate bis(dimethylamino)phosphine was heated under reflux with (*R*,*R*)-*N*,*N*′-dimethyl-1,2-diaminocyclohexane **2** until no further dimethylamine could be detected in the nitrogen stream from the reaction. At this point solvent removal provided the pure ligands **1**. Although always handled under an inert atmosphere when in solution, each of the ligands proved to be resistant to atmospheric oxidation when in solid form. Treatment of **1c** with borane–dimethyl sulfide resulted in formation of a highly stable borane complex (**3**) which was purified by chromatography. An X-ray crystallographic structure determination of **3** was carried out in order to confirm the identity of this compound (Fig. 1). We have in previous work on benzazaphospholidine ligands demonstrated that related borane complexes could be used as a method for the protection of ligands.[3] However, in the case of **3** all attempts to remove the borane resulted in decomposition of the ligand.

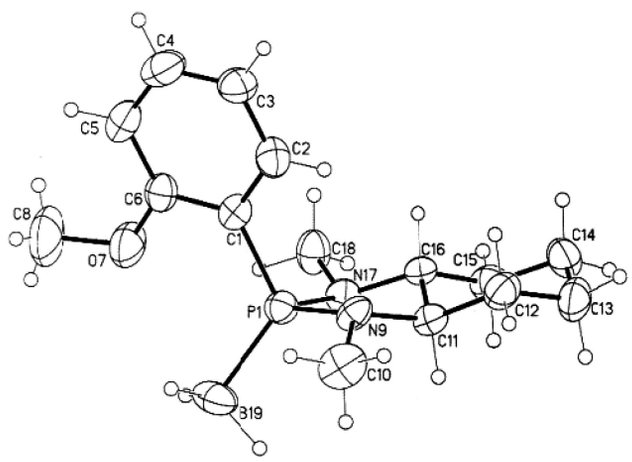


Fig. 1 X-Ray crystallographic structure of compound **3**.

We were also able to prepare the bis(diazaphospholidine) ligand **4** through the reaction of **2** with the known bis[bis(dimethylamino)phosphine] **5**. In this case the product was formed in

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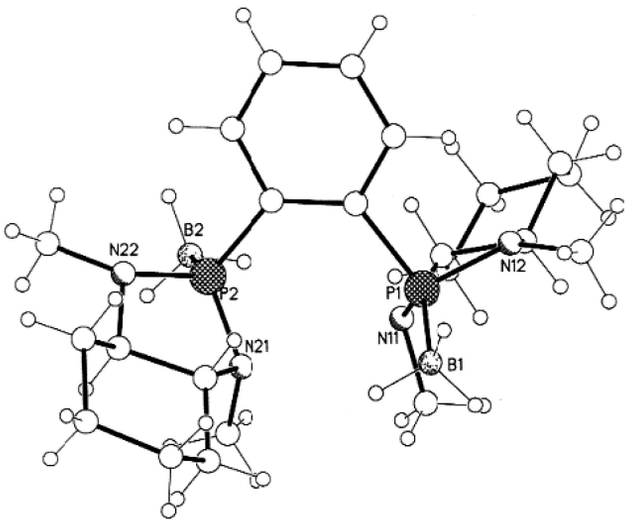
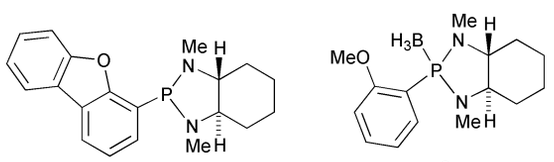
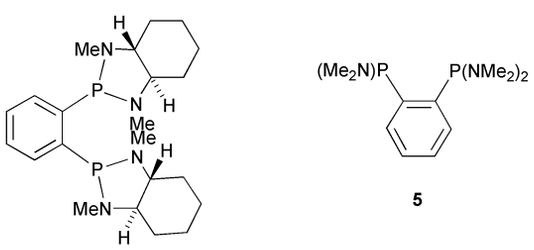
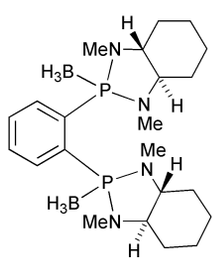


Fig. 2 X-Ray crystallographic structure of compound **6**.



88% yield. The ligand appeared to be stable if kept under an inert atmosphere, and structural evidence was obtained through an X-ray crystallographic structure of the diborane derivative **6** (formed in 91% yield, Fig. 2). Similar ligands to **6** have been described by Spilling[7] and Knochel,[8] the latter of whom reported that the borane groups could be removed using morpholine. In our hands, however, the ligands decomposed when we attempted this.



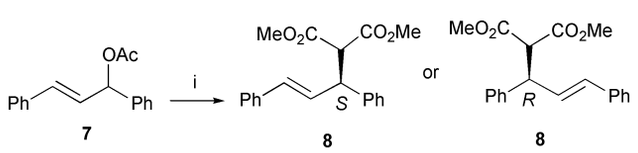


We have applied the series of ligands described above to the nucleophilic allylic substitution reactions of 1,3-diphenyl-3-acetoxyprop-1-ene **7** (Scheme 2).[2,9,10] *N*,*O*-Bis(trimethylsilyl)-acetamide (BSA) was chosen as the base to deprotonate dimethyl malonate because good results had been achieved using this method in previous work carried out in this group.[3] Finally a small amount of sodium acetate was added to the reaction as a catalytic base to activate the BSA and to enhance the dynamic kinetic resolution of racemic acetate **7**. In most cases the substitution reaction gave good yields of adduct **8** and good to excellent asymmetric inductions (Table 1). A general improvement and reversal of selectivity relative to the parent ligand **1a** is observed upon introduction of an *ortho*-substituent to the ligand. When 20 mol% of ligand **1c** and 5 mol% of allylpalladium chloride dimer (*i.e.* 10 mol% of Pd) were used in the alkylation reaction a 97% yield of **8** was achieved after stirring for 16 h at rt. The enantiomeric excess of the product was determined to be 89% (*R*) using the (+)-Eu(hfc)$_3$ chiral shift reagent method (hfc = 3-heptafluorobutyrylcamphorate). The level of electron density in the aromatic ring alone does not appear to influence the selectivity to any great extent (compare ligands **1a** and **1b**). Although the best results, 89% yield and 78% ee in favour of the (*R*)-enantiomer, were achieved using ligands **1c** and **1d** respectively, the same product enantiomer was obtained using ligands lacking *ortho*-groups with any potential to co-ordinate to the palladium (*i.e.* **1e** and **1f**). This suggests that all the *ortho*-substituted ligands may share a common mode for directing the asymmetric transformation. The importance of the size of the *ortho*-substituent is also difficult to gauge since the ethyl and isopropyl substituted ligands **1e** and **1f** gave similar enantioselectivities. Use of ligand **4** in the test reaction resulted in an enantioselectivity of 55% in favour of the (*R*)-enantiomer (87% yield). The reaction time was 3 days (in contrast to a reaction time of 16–24 hours for the monodonor ligands) and this indicated that the turnover of the catalytic palladium–ligand complex was slow, possibly due to steric hindrance.

One final, important, factor had to be considered before a model for the stereoinduction could be proposed. Lemaire *et al.* have recently reported the use of (*S*,*S*)-*trans*-*N*,*N*′-dimethyl-1,2-diphenylethylenediamine as a ligand for palladium-catalysed allylic alkylation, giving enantioselectivities of up to 95%.[11] The possibility that the diazaphospholidine ligands could be decomposing to liberate diamine **2** in the course of the alkylation reaction had to be addressed. In the event, use of diamine **2** as ligand in the alkylation reaction gave only a 6% yield of **8** with an enantiomeric excess of 15% (*S*). Clearly, even if some diamine was liberated during the alkylation reaction using the diazaphospholidine ligands, this could not account for the high levels of enantioselectivity previously achieved in the alkylation reactions.

The ligand to palladium ratio was varied to assess whether a 2 : 1 ratio, which we had initially employed, was essential to maintain the rate and stereoselectivity of the reaction. Use of a 1 : 1 ratio of ligand to palladium in the allylic alkylation reaction was observed to give a slightly impaired rate of alkylation and a minimal reduction in enantioselectivity to 83% (*R*), compared to 89% (*R*) when a 2 : 1 ratio was employed. This slight loss of enantioselectivity was probably caused by a reduction in the effective concentration of the active ligand–palladium complex present in solution.

Consideration was given to the palladium loading used in the alkylation reaction. Environmental and economic factors dictated that as little palladium as possible should be used in the reaction, but enough should be present to maintain the desired high levels of enantioselectivity. Reduction of the palladium loading to 5 mol% gave almost identical results with ligand **1c** (85% ee) to those obtained when 10 mol% was employed, however a further reduction to 2 mol% resulted in an slight reduction in selectivity (82% ee). Clearly the use of no lower than 5 mol% of palladium would be appropriate to enable the high levels of enantioselectivity to be maintained in future reactions.



Scheme 2 *Reagents and conditions*: i) $[(C_3H_5)PdCl]_2$, $CH_2(CO_2Me)_2$, BSA, NaOAc, DCM, ligand **1a**–**1i**.

Table 1 Asymmetric Pd-catalysed allylic substitution reactions using ligands **1a**–**1i**, **2**, **4**

Ligand	Ligand mol%	Pd atom mol%[a]	*t*/h	Yield **8** (%)	ee (%) (*R*/*S*)
1a	20	10	16	97	28 (*S*)
1b	20	10	16	71	23 (*S*)
1c	20	10	16	97	89 (*R*)
1c	10	10	20	89	83 (*R*)
1c	10	5	12	85	85 (*R*)
1c	4	2	20	94	82 (*R*)
1d	20	10	24	90	78 (*R*)
1e	20	10	16	84	59 (*R*)
1f	20	10	16	91	56 (*R*)
1g	20	10	24	85	66 (*R*)
1h	20	10	24	84	51 (*R*)
1i	20	10	20	92	35 (*R*)
4	20	10	72	87	55 (*R*)
2	20	10	24	6	15 (*S*)

[a] Corresponds to twice the mol% $[(C_3H_5)PdCl]_2$ employed.

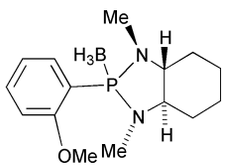


Fig. 3 Gearing of methyl groups on the nitrogen atoms in **3**.

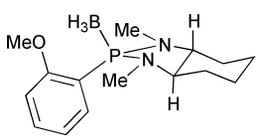


Fig. 4 Relative position of the methoxy group in **3**.

The effect of temperature was investigated. When the alkylation reaction was carried out at 0 °C product **8** was produced in 89% ee. There was also a slight reduction in the rate of reaction, which was to be expected.

At present, there is insufficient direct evidence to determine the means by which asymmetric induction is achieved. It would appear that whilst the introduction of an *ortho*-substituent in the ligand is crucial for high enantioselectivity, the observation of similar results from co-ordinating and non-co-ordinating groups suggests that the ligand is probably only attached to the palladium through the phosphorus atom.[12] This speculation is supported by observations and X-ray crystallographic structures of ligands such as 2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MOP), in which a proximal methoxy group does not bind to the metal.[12] More recent studies, however, have revealed that the *active catalyst* actually contains a bidentate MOP ligand, bound to metal through both the phosphorus atom and the naphthyl ring containing the methoxy group.[13] The implications of this discovery for our ligands remain to be established.

Of significance is the *pseudo*-C_2-symmetry of the ligands and potential participation of 'gearing' by the *N*-methyl groups with the adjacent chiral centres. Studies by others,[4,14] and our own X-ray crystal structure of the borane complexes reported herein indicate that in the monodonor ligands the nitrogen atoms are partially tetrahedral, the result of the methyl groups avoiding eclipsing interactions with the adjacent C–C bonds (Fig. 3). The X-ray crystal structure of **3** also reveals that the *ortho*-substituent favours a position away from the heterocyclic ring (Fig. 4). This suggests that steric interactions may prevent a 180° rotation about the P–C(aryl) bond. If this conformational preference is maintained in the palladium complex, then clearly this *ortho*-group may be projected into the region of the appended allylic group, and thus provide a means to influence the enantioselectivity of the reaction. How this effect is transferred to the asymmetric reaction, however, is at present unclear.† In the absence of an *ortho*-substituent the conformation of the ligand within the Pd complex may be quite different.

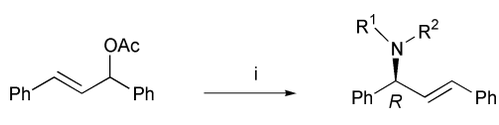
Table 2 Asymmetric allylic amination reactions[a]

Product	Solvent	*t*/h	Yield (%)	ee (%) (*R*/*S*)
9a	DCM	42	68	78 (*S*)
9a	THF	20	49	73 (*S*)
9a	THF	5	77	68 (*S*)
9b	DCM	168	67	78 (*S*)
9b	THF	8	51	61 (*S*)
9c	THF	8	67	61 (*S*)
9d	DCM	64	45	76 (*S*)
9e	DCM	41	48	68 (*S*)
9f	DCM	16	63	58 (*S*)

[a] All reactions were carried out at room temperature.

The X-ray crystallographic structure of **6** revealed that two of the four methyl groups on the nitrogen atoms are in pseudo-axial positions, in sharp contrast to the situation with **3**. This may be the result of the avoidance of an unfavourable steric clash by an otherwise pseudo-equatorial methyl group with the neighbouring diazaphospholidine group. This suggests that the *N*-methyl groups are not strongly locked in specific conformational locations in this class of ligand. Although we do not have direct evidence, such as an X-ray crystallographic structure of a complex, we believe that **4** is likely to operate as a bidentate ligand, *i.e.* with both phosphorus atoms chelated to the metal atom.

Having identified **1c** as the best of the series of ligands, we extended our studies to nitrogen nucleophiles (Scheme 3, Table 2). Literature precedent indicated that benzylamine was a good nucleophile in the allylic amination reaction, in some cases giving aminated products with a high degree of enantioselectivity.[15] The use of benzylamine as nucleophile in the



7 **9a-f**

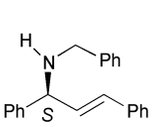
Scheme 3 *Reagents and conditions*: i) 2.5 mol% $[(C_3H_5)PdCl]_2$, R^1R^2NH, BSA, NaOAc, DCM or THF, 10 mol% ligand **1c**.

† A referee has suggested that restricted rotation about the P–C(aryl) bond, controlled *via* a 'propeller' effect involving a twist of C2 away from the raised methyl on N17, may be important to the stereodirecting effect of the ligand.

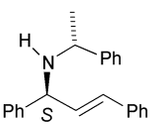
amination of 1,3-diphenyl-3-acetoxyprop-1-ene **7** in the presence of catalytic amounts of ligand **1c**, allylpalladium chloride dimer and sodium acetate in a DCM solution at rt gave the desired amine **9a** in 68% yield after stirring for 42 h. The enantiomeric excess was determined to be 78% (*S*) by chiral HPLC analysis using a Chiralcel OD column. [The sample was determined to be enriched with the (*S*)-isomer by comparison of the sign of the optical rotation and retention time measured by HPLC with literature examples.] Although the amination reaction proceeded at a reduced rate compared to the analogous alkylation reaction, the high degree of stereoinduction, in the same sense, suggests that the substitution proceeded *via* the same mechanism.

The use of THF as solvent served to improve the rate of reaction to some extent, giving amine **9a** in 49% yield after 20 h, but with a slight drop in enantioselectivity to 73%. When the amination was carried out in THF at 50 °C a dramatic improvement in the rate was observed giving amine **9a** in 77% yield after only 5 h but this was also accompanied by a 10% drop in enantiomeric excess.

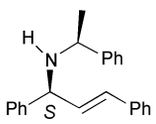
In order to assess whether there would be any effect of a chiral centre within the nucleophile on the enantioselectivity of the amination reaction the use of α-methylbenzylamine as a nucleophile was investigated. In our first experiment aminated product **9b** was formed in 67% yield after stirring at rt in DCM for 168 h. The diastereomeric excess was measured by NMR analysis to be 78% in favour of the (*S*)-enantiomer. The possibility of match/mismatch effects of chirality present in the ligand and the chiral amine was investigated by setting up two parallel reactions using both the (*R*)-(+)- and (*S*)-(−)-isomers of α-methylbenzylamine under identical reaction conditions. Stirring for 8 h in THF at 50 °C gave amine **9b** in 51% yield and 61% de compared to **9c** which was produced in 67% yield and the same de. Clearly the chiral centre present in the nucleophile was having no effect on the enantioselectivity of the amination reaction.



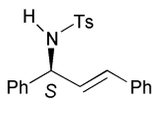
9a



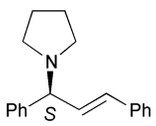
9b



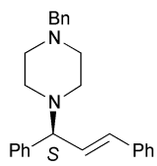
9c



9d



9e



9f

From the results obtained thus far it was clear that the best enantioselectivities for the amination reaction were achieved by using DCM as solvent at rt. It was decided that the sluggish rate of the reaction under these conditions could be tolerated so long as the enantioselectivity of the reaction remained at reasonable levels. The sodium salt of toluene-*p*-sulfonamide as nucleophile in the substitution of **7** using diazaphospholidine ligand **1c** gave the desired allyl sulfonamide **9d** in a low (45%) yield but with a disappointing enantiomeric excess of 76%, no better than the case for benzylamine under analogous conditions.

When pyrrolidine was employed as the nucleophile in the allylic amination with**1c**, the desired allylic amine **9e** was produced in 48% yield, as a highly crystalline solid. The enantiomeric excess was measured by HPLC analysis to be 68% in favour of the (*S*)-isomer (presumed by analogy with the other results obtained using **1c**). Similarly *N*-benzylpiperazine yielded 63% of the crystalline, allylic amine **9f** with an enantioselectivity of 58% ee in favour of the (*S*)-isomer, again determined by HPLC analysis. The lower level of enantioselectivity achieved in this case was a little disappointing.

In conclusion, a novel class of diazaphospholidine ligands has been synthesised and their application to palladium-catalysed allylic substitution has been demonstrated. Ongoing work is directed towards the synthesis of improved ligands based on this general class for a variety of transition metal catalysed asymmetric transformations.

Experimental

General

THF and ether were distilled from their corresponding sodium benzophenone ketals. Toluene was distilled from sodium. DCM was distilled from calcium hydride. Methanol was distilled from activated magnesium sulfate. DMF was distilled under reduced pressure (water aspirator) from anhydrous magnesium sulfate and stored over 4 Å molecular sieves. All other solvents were used as supplied unless otherwise stated. Petrol refers to petroleum ether with a boiling range of 60–80 °C. Rt refers to ambient room temperature normally between 18–22 °C. 0 °C refers to an ice slush bath. −78 °C refers to an acetone–CO_2 bath. Heating experiments were carried out using thermostatically controlled oil baths. All air- and moisture-sensitive reactions were carried out in flame- or oven-dried Schlenk apparatus and under a dry nitrogen or argon atmosphere. Larger scale reactions (>1 g) were carried out in two- or three-necked round-bottom flasks fitted with appropriate gas inlet adapters. All reactions were monitored using foil or plastic backed commercially available 0.25 mm silica gel plates (Merck) and visualised using $UV_{254\ nm}$ and ceric ammonium nitrate, polymolybdenic acid, ninhydrin, permanganate or iodine dips as appropriate. Flash column chromatography was carried out using 60 Å silica gel (Merck) unless otherwise stated. All solid products were pre-absorbed onto silica, oils were dissolved in a minimal amount of the eluent and pipetted onto the column surface. Chiral HPLC analyses were carried out on a Waters HPLC system using a Chiralcel OD column. Most compounds were used as supplied by Aldrich, Fluka or Lancaster. Triethylamine and TMEDA were distilled from calcium hydride and stored over potassium hydroxide pellets under a nitrogen atmosphere. *tert*-Butyl alcohol was dried over activated calcium sulfate and distilled under nitrogen before use.

Infrared spectra were recorded as Nujol mulls or chloroform films between sodium chloride plates using a Perkin-Elmer 1310 FTIR spectrophotometer. NMR spectra were recorded for $CDCl_3$ or DMSO-d_6 solutions using a Bruker AC250 250 MHz or a Bruker ACF400 400 MHz spectrometer. All chemical shifts (δ) are measured in ppm downfield of tetramethylsilane as internal reference. Coupling constants (J) are measured in Hz. Abbreviations for splitting patterns are as follows: (s) singlet, (bs) broad singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet. DEPT techniques were commonly used to aid interpretation of ^{13}C spectra, for which C–P couplings are quoted. In some cases distinct P-coupled ^{13}C peaks could not be assigned with confidence and in these cases the observed peaks are listed. ^{31}P spectra were proton-decoupled. Mass spectra were recorded on a 7070E VG mass spectrometer for all EI and CI spectra. FAB and HRMS spectra were recorded by the EPSRC Mass Spectrometry Service at Swansea. Microanalysis was performed using a Carlo Erba elemental analyser (MOD 1106). Optical rotations were recorded using a Perkin-Elmer polarimeter (sodium D line) and a 1 cm rotation cell, values for $[\alpha]_D$ are given in 10^{-1} deg cm^2 g^{-1} at the specified temperature.

(3a*R*,7a*R*)-1,3-Dimethyl-2-phenyl-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 1a

Phenylbis(dimethylamino)phosphine[5b] (103 mg, 0.53 mmol) was dissolved in toluene (2.0 mL, degassed), (*R*,*R*)-*N*,*N*′-

dimethyl-1,2-diaminocyclohexane **2** (75 mg, 0.53 mmol) was added and the mixture heated to reflux for 2 days. The solvent was then evaporated to give **1a** as a pale yellow oil (130 mg, 100%). $[a]_D^{20}$ = +31.4 (*c* = 1.25, $CHCl_3$); ν_{max}(liquid film)/cm^{-1} 1460 (P–Ar), 1024 (P–N); δ_H (250 MHz, $CDCl_3$) 7.57–7.50 (2H, m, ArH), 7.40–7.33 (3H, m, ArH), 2.76 (3H, d, *J* 15.4, CH_3), 2.21 (3H, d, *J* 15.7, CH_3), 2.20–2.17 (2H, m, CH), 1.92–1.74 (3H, m, $(CH_2)_4$), 1.33–1.09 (5H, m, $(CH_2)_4$); δ_C (60 MHz, $CDCl_3$) 138.9 (C*i*, J_{C-P} 46.3), 131.0 (CH, J_{C-P} 19.6), 128.9 (CH), 127.3 (CH), 70.7 (CH, J_{C-P} 4.9), 65.3 (CH, J_{C-P} 7.9), 36.8 (CH_3, J_{C-P} 35.4), 30.6 (CH_3, J_{C-P} 8.8), 30.0 (CH_2), 28.6 (CH_2), 24.3 (CH_2), 23.9 (CH_2); δ_P (160 MHz, $CDCl_3$) 111.74 (s); *m*/*z* (CI) 249 (MH^+, 71%) (Found: 249.1521. $C_{14}H_{21}N_2P$ requires MH^+, 249.15206).

Synthesis of *p*-methoxyphenylbis(dimethylamino)phosphine

tert-Butyllithium (40.8 mL, 69.4 mmol) was added to a solution of 4-bromoanisole (4.3 mL, 35 mmol) in diethyl ether (100 mL) at −70 °C. After the addition was complete the temperature of the solution was maintained for 1 h. In a separate vessel, hexamethylphosphorus triamide (4.2 mL, 23.1 mmol) was added dropwise to phosphorus trichloride (1.0 mL, 11.6 mmol) at 0 °C. The mixture was heated to 70 °C for 30 min to ensure complete redistribution to form bis(dimethylamino)chlorophosphine; it was then cooled to −70 °C and the lithiate was added dropwise. After the addition the reaction mixture was allowed to warm up overnight. Sodium bicarbonate (1 g) mixed with dichloromethane (5 mL) was added and the mixture stirred for 1 h. The solution was filtered under nitrogen to remove the inorganic salts and the solvent was removed by use of a high vacuum pump. The residue was distilled under vacuum to yield *p*-methoxyphenylbis(dimethylamino)phosphine (bp 100 °C, 0.4 mmHg) (2.92 g, 37%) as a colourless oil; ν_{max}(thin film)/cm^{-1} 1443 (Ar–P), 1062 (P–N); δ_H (400 MHz, C_6D_6) 7.48–7.42 (2H, m, ArH), 6.95–6.85 (2H, m, ArH), 3.39 (3H, s, OCH_3), 2.71 (12H, d, *J* 9, 2 × $N(CH_3)_2$); δ_C (62.8 MHz, C_6D_6) 159.9 (C*i*), 132.85 (C*i*, J_{C-P} 16), 132.32 (ArCH, J_{C-P} 5.7), 114.38 (ArCH, J_{C-P} 4), 54.66 (OCH_3), 41.54 (2 × $N(CH_3)_2$, J_{C-P} 15.7); δ_P (161 MHz, C_6D_6) 102.2; *m*/*z* (EI) 226 (M^+, 22), 182 (61), 140 (9), 139 (100), 77 (15), 76 (23), 60 (27), 44 (16), 42 (46%) (Found: 226.1235. $C_{11}H_{19}N_2O_1P_1$ requires M^+, 226.1234).

Synthesis of (3a*R*,7a*R*)-1,3-dimethyl-2-*p*-methoxyphenyl-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 1b

(*R*,*R*)-*N*,*N*′-Dimethyl-1,2-diaminocyclohexane **2** (67 mg, 0.473 mmol) was added to solution of *p*-methoxyphenylbis(dimethylamino)phosphine (108 mg, 0.473 mmol) in toluene (2 mL) at rt. The reaction mixture was stirred at reflux with a constant stream of nitrogen to allow the venting of dimethylamine as the reaction proceeded. After 3 days the outflow was non-basic, and the reaction mixture was allowed to cool. Removal of the toluene left **1b** (127 mg, 96%) as a viscous clear oil. $[a]_D^{20}$ +72.8 (*c* = 1.25, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 1462 (Ar–P), 1026 (P–N); δ_H (400 MHz, C_6D_6) 7.68 (2H, m, ArH), 6.94 (2H, d, *J* 8.4 ArH), 3.38 (3H, s, OCH_3), 2.72 (3H, d, *J* 16, $N(CH_3)$), 2.23 (3H, d, *J* 15, $N(CH_3)$), 2.5–2.0 (3H, m, 2 × CH + $(CH_2)_4$), 1.8–0.8 (7H, m, $(CH_2)_4$); δ_C (100 MHz, C_6D_6) 161.26 (ArC), 135.0 (ArC, J_{C-P} 9.6), 133.27 (ArC, J_{C-P} 21), 113.53 (ArC, J_{C-P} 6), 71.4 (CH, J_{C-P} 3.2), 65.75 (CH, J_{C-P} 9.6), 54.7 (OCH_3), 37.23 (CH_3, J_{C-P} 36.9), 30.8 (CH_3, J_{C-P} 11), 30.5 (CH_2), 29.15 (CH_2, J_{C-P} 3), 24.72 (CH_2), 24.44 (CH_2); δ_P (161 MHz, C_6D_6) 112.6; *m*/*z* (CI) 278 (M^+, 65), 245 (50), 171 (90), 141 (100), 112 (68), 83 (25), 70 (55%) (Found: 278.1547. $C_{15}H_{23}N_2O_1P_1$ requires M^+, 278.1548).

o-Methoxyphenylbis(dimethylamino)phosphine [16]

o-Anisole (5.0 g, 46.3 mmol) was dissolved in THF (30.0 mL) and cooled to −78 °C. *n*-BuLi (19.4 mL, 48.6 mmol of a 2.5 M solution in hexanes) was added slowly, dropwise. The mixture was then allowed to warm to rt for 3 h. In a separate vessel, PCl_3 (1.3 mL, 15.3 mmol) was cooled to 0 °C and HMPT (5.6 mL, 31 mmol) was added slowly, dropwise. After the vigorous, fuming reaction had subsided the mixture was heated to 70 °C for 30 min. The colourless oil was allowed to cool to rt and diluted with THF (10.0 mL). The lithiated anisole was recooled to −78 °C and the solution of $ClP(NMe_2)_2$ was added *via* cannula. The pale yellow solution was stirred at −78 °C for 3 h and then allowed to stir at rt overnight. The reaction was quenched by the addition of sodium bicarbonate solution and the aqueous phase extracted with DCM (3 × 50 mL). The combined organic extracts were dried over potassium carbonate, filtered and the solvent was evaporated to give an orange oil. Purification by fractional distillation gave the product as a colourless oil (5.0 g, 50%). δ_H (250 MHz, $CDCl_3$) 7.38–7.33 (1H, m, ArH), 7.31–7.24 (1H, m, ArH), 7.00–6.93 (1H, m, ArH), 6.87–6.82 (1H, m, ArH), 3.83 (3H, s, CH_3), 2.69–2.65 (12H, d, *J* 9.6, $(NMe_2)_2$); δ_P (160 MHz, $CDCl_3$) 96.5. These data matched those reported previously for this compound.[16]

(3a*R*,7a*R*)-1,3-Dimethyl-2-*o*-methoxyphenyl-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 1c

o-Methoxyphenylbis(dimethylamino)phosphine (160 mg, 0.71 mmol) was dissolved in toluene (2.0 mL, degassed) and to this was added (*R*,*R*)-*N*,*N*′-dimethyl-1,2-diaminocyclohexane **2** (100 mg, 0.71 mmol). The mixture was heated to reflux and stirred for 3 days. After this time the solvent was evaporated to give **1c** as pale cream crystals after drying under high vacuum (197 mg, 100%). $[a]_D^{20}$ = +110 (*c* = 1.2, $CHCl_3$); ν_{max}(liquid film)/cm^{-1} 2937 (Ar–OCH_3), 1461 (P–Ar), 1025 (P–N); δ_H (250 MHz, $CDCl_3$) 7.56–7.52 (1H, m, ArH), 7.34–7.27 (1H, m, ArH), 6.99–6.93 (1H, m, ArH), 6.87–6.82 (1H, m, ArH), 3.85 (3H, s, OCH_3), 2.72 (3H, d, *J* 15.7, NCH_3), 2.36 (3H, d, *J* 15.4, NCH_3), 2.35–2.29 (1H, m, CH), 2.23–2.17 (2H, m, CH + $(CH_2)_2$), 1.95–1.91 (1H, m, $(CH_2)_2$), 1.82–1.74 (2H, m, $(CH_2)_2$), 1.32–1.09 (4H, m, $(CH_2)_2$); δ_C (100 MHz, $CDCl_3$) 162.0 (C*i*, J_{C-P} 16.5), 132.5 (CH), 130.3 (CH), 127.5 (C*i*), 119.7 (CH), 109.7 (CH), 70.7 (CH, J_{C-P} 4.9), 65.7 (CH, J_{C-P} 9.1), 55.1 (CH_3), 37.0 (CH_3, J_{C-P} 37.6), 31.0 (CH_3, J_{C-P} 7.7), 30.1 (CH_2), 28.6 (CH_2, J_{C-P} 2.9), 24.4 (CH_2), 24.0 (CH_2); δ_P (160 MHz, $CDCl_3$) 103.87; *m*/*z* (EI) 278 (M^+, 45%) (Found: 278.1548. $C_{15}H_{23}N_2OP$ requires M, 278.1548).

(3a*R*,7a*R*)-1,3-Dimethyl-2-*o*-methoxyphenyl-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole P–borane complex 3

o-Methoxyphenylbis(dimethylamino)phosphine (220 mg, 0.97 mmol) was dissolved in toluene (2.0 mL, degassed) and (*R*,*R*)-*N*,*N*′-dimethyl-1,2-diaminocyclohexane **2** (138 mg, 0.97 mmol) was added with stirring at rt. The mixture was heated to reflux, with an N_2 bubbler attached, for 32 h, until the N_2 outflow was of neutral pH. The mixture was then allowed to cool to rt and borane–dimethyl sulfide (0.15 mL, 10 M) was added dropwise. After 2 h the reaction was quenched by the addition of sodium bicarbonate solution and the aqueous phase extracted with DCM (3 × 10 mL). The combined organic extracts were dried over sodium sulfate, filtered and the solvent evaporated. Purification by flash chromatography on silica eluted with 10% ethyl acetate–petrol gave **3** as a white solid (145 mg, 50%). Mp 96–98 °C (from ethyl acetate–hexane); $[a]_D^{20}$ = +6.3 (*c* = 1, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 7.80–7.71 (1H, m, ArH), 7.47–7.42 (1H, m, ArH), 7.03–6.97 (1H, m, ArH), 6.94–6.89 (1H, dd, *J* 8.1, 4.4, ArH), 3.85 (3H, s, OCH_3), 2.60 (3H, d, *J* 12.5, NCH_3), 2.51 (2H, m, CHCH), 2.45 (3H, d, *J* 13.7, NCH_3), 2.17 (1H, m, C_4H_8), 2.04 (1H, m, C_4H_8), 1.83 (2H, m, C_4H_8), 1.28–1.23 (4H, m, C_4H_8); δ_C (100 MHz, $CDCl_3$) 161.1 (C*i*, J_{C-P} 5.0), 135.0 (CH, J_{C-P} 10.7), 133.3 (CH), 120.5 (C*i*), 120.2 (CH, J_{C-P} 9.4), 111.1 (CH, J_{C-P} 4.6), 67.5 (CH), 64.5 (CH), 55.3 (CH_3), 31.5 (CH_3, J_{C-P} 9.1), 29.3 (CH_3, J_{C-P} 2.9), 28.8 (CH_2, J_{C-P} 4.9), 28.3 (CH_2, J_{C-P} 8.1), 24.1 (CH_2), 24.0 (CH_2);

δ_P (160 MHz, $CDCl_3$) 107.2 (m); *m*/*z* (CI) 293 (MH^+, 23%), 279 ($MH - BH_3^+$, 90) (Found: 293.1954. $C_{15}H_{26}N_2OPB$ requires MH, 293.1954). An X-ray quality crystal was produced by slow dispersion of hexane into an ethyl acetate solution of **3**.

Synthesis of *o*-methylthiophenylbis(dimethylamino)phosphine

n-Butyllithium (5.8 mL, 0.013 mol, 2.2 M in hexanes) was added to a solution of 2-bromothioanisole (2.59 g, 0.0127 mol) in diethyl ether (100 mL) at −20 °C. After 30 min at this temperature, anhydrous zinc dichloride (1.74 g, 0.0127 mol) was added in small portions. The reaction mixture was allowed to warm to 0 °C, stirred for 30 min at 0 °C and then re-cooled to −70 °C. Phosphorus trichloride (1.14 mL, 0.0127 mol) was added dropwise and the reaction mixture was allowed to warm up overnight. Dimethylamine was bubbled through the solution until the aryl–PCl_2 (^{31}P 147 ppm) compound was completely converted to the aryl–$P(NMe_2)_2$ (^{31}P 96 ppm). Deoxygenated water (20 mL) was added to the solution and the organic layer was drawn off, dried over anhydrous magnesium sulfate, filtered under nitrogen and the solvent was removed by use of a high vacuum pump. The residue was distilled under vacuum to yield the product as a viscous clear oil (bp 100 °C, 0.4 mmHg) (1.51 g, 48%); ν_{max}(thin film)/cm^{-1} 1438 (Ar–P), 1041 (P–N); δ_H (400 MHz, C_6D_6) 7.62–7.58 (1H, m, ArH), 7.15–7.04 (3H, m, ArH), 2.72 (12H, d, *J* 8.7, (2 × $N(CH_3)_2$), 2.04 (3H, s, SCH_3); δ_C (100 MHz, C_6D_6) 143.1 (Ar, J_{P-C} 22.4), 139.18 (Ar, J_{P-C} 5), 131.45 (Ar, J_{P-C} 8), 128.4 (Ar), 125.27 (Ar), 123.96 (Ar), 41.35 ($N(CH_3)_2$, J_{P-C} 17), 16.0 (CH_3); δ_P (161 MHz, C_6D_6) 96.3; *m*/*z* (EI) 242 (M^+, 25), 227 (30), 198 (94), 155 (52), 153 (100), 139 (35), 107 (25), 63 (30), 44 (37%) (Found: 242.1007. $C_{11}H_{19}N_2S_1P_1$ requires M^+, 242.1023).

Synthesis of (3a*R*,7a*R*)-1,3-dimethyl-2-*o*-methylthiophenyl-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 1d

(*R*,*R*)-*N*,*N*′-Dimethyl-1,2-diaminocyclohexane **2** (36.8 mg, 0.260 mmol) was added to a solution of *o*-methylthiophenylbis(dimethylamino)phosphine (63.4 mg, 0.260 mmol) in toluene (3 mL) at rt. The reaction mixture was stirred at reflux with a constant stream of nitrogen to allow the venting of dimethylamine as the reaction proceeded. After 3 days the outflow was non-basic and the reaction mixture was allowed to cool. Removal of the toluene left **1d** (75 mg, 98%) as a white viscous liquid. $[\alpha]_D^{20}$ +90.47 (*c* = 1.05, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 1442 (Ar–P), 1023 (P–N); δ_H (400 MHz, C_6D_6) 7.94–7.90 (1H, dt, *J* 8 and 2, ArH), 7.2–7.1 (3H, m, ArH), 2.70 (3H, d, *J* 15, $N(CH_3)$), 2.65 (3H, d, *J* 15, $N(CH_3)$), 2.6–2.2 (3H, m, aliphatic), 2.15 (3H, s, SCH_3), 2.0–0.8 (7H, m, aliphatic); δ_C (62.8 MHz, C_6D_6) 143.58 (C*i*, J_{P-C} 26.5), 141.45 (C*i*, J_{P-C} 44.3), 131.84 (ArCH, J_{P-C} 3), 129.59 (ArCH), 128.54 (ArCH), 124.8 (ArCH), 70.05 (CH, J_{P-C} 4), 65.84 (CH, J_{P-C} 7.8), 37.39 (CH_3, J_{P-C} 38.4), 32.54 (CH_3, J_{P-C} 13.8), 30.8 (CH_2), 28.86 (CH_2), 24.77 (CH_2), 24.57 (CH_2), 17.72 (SCH_3, J_{P-C} 8.8); δ_P (161 MHz, C_6D_6) 107.2 (Found: 294.1320. $C_{15}H_{23}N_2PS$ requires M^+, 294.1320).

Synthesis of 2-ethylphenylbis(dimethylamino)phosphine

n-Butyllithium (5.2 mL, 0.013 mol, 2.5 M in hexanes) was added to a solution of 2-iodoethylbenzene (3.0 g, 0.013 mol) in diethyl ether (80 mL) at −40 °C. The solution was allowed to warm to −20 °C for 1 h and then re-cooled to −70 °C. In a separate vessel, hexamethylphosphorus triamide (1.55 mL, 0.00851 mol) was added dropwise to phosphorus trichloride (0.38 mL, 0.0043 mol) at 0 °C. The mixture was heated to 70 °C for 30 min to ensure complete redistribution to form bis-(dimethylamino)chlorophosphine. The mixture was re-cooled to rt and added dropwise to the lithiate at −70 °C. The reaction mixture was allowed to reach rt overnight. Deoxygenated water (10 mL) was added and the organic layer was removed, dried over anhydrous magnesium sulfate, filtered under nitrogen and the solvent was removed using a high vacuum pump. The resulting oil was distilled under vacuum to yield the product (bp 95 °C, 0.4 mmHg) (2.514 g, 86%) as a colourless oil; ν_{max}(thin film)/cm^{-1} 1462 (Ar–P), 1058 (P–N); δ_H (250 MHz, C_6D_6) 7.68–7.62 (1H, m, ArH), 7.27–7.23 (3H, m, ArH), 2.87 (2H, q, *J* 8, CH_2), 2.64 (12H, d, *J* 9, (2 × $N(CH_3)_2$), 1.29 (3H, t, *J* 8, CH_3); δ_C (62.8 MHz, C_6D_6) 146.7 (C*i*, J_{P-C} 21.6), 138.7 (C*i*, J_{P-C} 8.8), 131 (ArCH, J_{P-C} 6), 129.5 (ArCH, J_{P-C} 2), 129.1 (ArCH), 125.6 (ArCH), 41.6 ($N(CH_3)_2$, J_{P-C} 17), 26.6 (CH_2, *J* 12.8), 14.9 (CH_3, *J* 3); δ_P (161 MHz, C_6D_6) 99.5; *m*/*z* (EI) 224 (M^+, 15), 180 (40), 179 (25), 133 (35), 119 (30), 109 (33), 91 (30), 76 (47), 42 (100%) (Found: 224.1442. $C_{12}H_{21}N_2P_1$ requires M^+, 224.1442).

Synthesis of (3a*R*,7a*R*)-1,3-dimethyl-2-(2-ethylphenyl)-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 1e

(*R*,*R*)-*N*,*N*′-Dimethyl-1,2-diaminocyclohexane **2** (45 mg, 0.32 mmol) was added to solution of 2-ethylphenylbis(dimethylamino)phosphine (72 mg, 0.32 mmol) in toluene (3 mL) at rt. The reaction mixture was stirred at reflux with a constant stream of nitrogen to allow the venting of dimethylamine as the reaction proceeded. After 2 days the outflow was non-basic, and the reaction mixture was allowed to cool. Removal of the toluene left **1e** (84 mg, 96%) as a viscous oil. $[\alpha]_D^{20}$ +51.6 (*c* = 0.6, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 1462 (Ar–P), 1026 (P–N); δ_H (250 MHz, C_6D_6) 7.92–7.87 (1H, m, ArH), 7.3–7.1 (3H, m, ArH), 3.5–3.3 (1H, m, $CHCH_3$), 3.0–2.8 (1H, m, $CHCH_3$), 2.66 (3H, d, *J* 15.1, $N(CH_3)$), 2.36 (3H, d, *J* 17.6, $N(CH_3)$), 2.6–2.0 (3H, m, aliphatic), 1.29 (3H, t, *J* 7, CH_2CH_3), 1.65–0.8 (7H, m, aliphatic); δ_C (62.8 MHz, C_6D_6) 148.27 (C*i*, J_{P-C} 26), 138.7 (C*i*, J_{P-C} 41.5), 131.4 (ArCH, J_{P-C} 3), 129.33 (ArCH), 128.74 (ArCH, J_{P-C} 3), 125.0 (ArCH), 69.5 (CH, J_{P-C} 4), 65.67 (CH, J_{P-C} 4), 37.45 (CH_3, J_{P-C} 37.1), 32.58 (CH_3, J_{P-C} 15.7), 30.75 (CH_2), 28.84 (CH_2), 24.77 (CH_2), 26.5 (CH_2CH_3), 24.50 (CH_2), 16.0 (CH_2CH_3); δ_P (161 MHz, C_6D_6) 109.9 (Found: 276.1760. $C_{16}H_{25}N_2P$ requires M^+, 276.1755).

Synthesis of 2-isopropylphenylbis(dimethylamino)phosphine

n-Butyllithium (8.1 mL, 0.020 mol, 2.5 M in hexanes) was added to a solution of 2-isopropyliodobenzene (5.0 g, 0.0203 mol) in diethyl ether (170 mL) at −10 °C. After 45 min at this temperature, anhydrous zinc dichloride (2.77 g, 0.0203 mol) was added in small portions. The reaction mixture was allowed to warm to 0 °C, stirred for 30 min at 0 °C and then re-cooled to −70 °C. Phosphorus trichloride (1.8 mL, 0.020 mol) was added dropwise and the reaction mixture was allowed to warm up overnight. Dimethylamine was bubbled through the solution until the aryl–PCl_2 (^{31}P 148 ppm) compound was completely converted to the aryl–$P(NMe_2)_2$ (^{31}P 99.5 ppm). Deoxygenated water (30 mL) was added to the solution and the organic layer was drawn off, dried over anhydrous magnesium sulfate, filtered under nitrogen and the solvent was removed by use of a high vacuum pump. The residue was distilled under vacuum to yield the product (bp 80–85 °C, 0.4 mmHg) (1.759 g, 36%) as a viscous clear oil. ν_{max}(thin film)/cm^{-1} 1444 (Ar–P), 1062 (P–N); δ_H (250 MHz, C_6D_6) 7.75–7.6 (1H, m, ArH), 7.36–7.23 (3H, m, ArH), 3.9–3.75 (1H, m, $CH(CH_3)_2$), 2.63 (12H, d, *J* 8.7, 2 × $N(CH_3)_2$), 1.29 (6H, d, *J* 6.7, $(CH_3)_2$); δ_C (62.8 MHz, C_6D_6) 151.87 (C*i*, J_{P-C} 20.6), 138.11 (C*i*, J_{P-C} 9.8), 130.67 (ArCH, J_{P-C} 5.9), 128.92 (C*i*), 126.1 (ArCH, J_{P-C} 3), 125.6 (ArCH), 41.4 (2 × $N(CH_3)_2$, J_{P-C} 16.7), 30.04 ($CH(CH_3)_2$, J_{P-C} 16.7), 24.3 ($CH(CH_3)_2$); δ_P (161 MHz, C_6D_6) 99.5; *m*/*z* (EI) 238 (M^+, 19), 194 (75), 193 (71), 149 (100), 133 (40), 76 (30), 44 (63%) (Found: 238.1599. $C_{13}H_{23}N_2P_1$ requires M^+, 238.1598).

Synthesis of (3a*R*,7a*R*)-1,3-dimethyl-2-(2-isopropylphenyl)-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 1f

(*R*,*R*)-*N*,*N*′-Dimethyl-1,2-diaminocyclohexane **2** (36 mg, 0.254 mmol) was added to a solution of 2-isopropylphenyl-

bis(dimethylamino)phosphine (61 mg, 0.254 mmol) in toluene (3 mL) at rt. The reaction mixture was stirred at reflux with a constant stream of nitrogen to allow the venting of dimethylamine as the reaction proceeded. After 3 days the outflow was non-basic, and the reaction mixture was allowed to cool. Removal of the toluene left **1f** (74 mg, 100%) as a glassy solid. $[\alpha]_D^{20}$ +29.71 (c = 1.75, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 1461 (Ar–P), 1024 (P–N); δ_H (400 MHz, C_6D_6) 7.96–7.92 (1H, m, ArH), 7.35–7.25 (3H, m, ArH), 4.28–4.18 (1H, m, C*H*$(CH_3)_2$), 2.71 (3H, d, *J* 15.1, N(CH_3)), 2.42 (3H, d, *J* 16.5, N(CH_3)), 2.6–2.0 (3H, m, aliphatic), 1.38 (6H, dd, *J* 7 and 3, CH(C*H*$_3)_2$), 1.8–0.9 (7H, m, aliphatic); δ_C (62.8 MHz, C_6D_6) 153.2 (C*i*, J_{P-C} 21.66), 137.63 (C*i*, J_{P-C} 42.3), 131.48 (ArCH, J_{P-C} 3), 129.59 (ArCH), 125.7 (ArCH, J_{P-C} 3), 125.05 (ArCH), 69.65 (CH, J_{P-C} 4), 65.5 (CH, J_{P-C} 7.8), 37.74 (CH_3, J_{P-C} 37.4), 32.51 (CH_3, J_{P-C} 14.7), 30.75 (CH_2), 30.08 (*C*H$(CH_3)_2$, J_{P-C} 23.6), 28.89 (CH_2, J_{P-C} 2), 25.12 (CH*C*H$_3$), 24.79 (CH_2), 24.58 (CH_2), 23.61 (CH*C*H$_3$); δ_P (161 MHz, C_6D_6) 110.8; *m*/*z* (EI) 290 (M^+, 20), 171 (100), 133 (30), 70 (35), 42 (40%) (Found: 290.1912. $C_{17}H_{27}N_2P_1$ requires M^+, 290.1911).

Synthesis of (3a*R*,7a*R*)-1,3-dimethyl-2-(2-bromophenyl)-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 1g

(*R*,*R*)-*N*,*N*′-Dimethyl-1,2-diaminocyclohexane **2** (47.6 mg, 0.335 mmol) was added to solution of 2-bromophenylbis-(dimethylamino)phosphine (92.9 mg, 0.335 mmol) in toluene (4 mL) at rt. The reaction mixture was stirred at reflux with a constant stream of nitrogen to allow the venting of dimethylamine as the reaction proceeded. After 2 days the outflow was non-basic, and the reaction mixture was allowed to cool. Removal of the toluene left **1g** (106 mg, 97%) as a white semi-solid. $[\alpha]_D^{20}$ +42.0 (c = 0.5, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 1460 (Ar–P), 1020 (P–N); δ_H (400 MHz, C_6D_6) 7.81 (1H, d, *J* 6, ArH), 7.45 (1H, d, *J* 6, ArH), 7.13 (1H, t, *J* 6, ArH), 6.82 (1H, t, *J* 6, ArH), 2.60 (3H, d, *J* 10.8, N(CH_3)), 2.57 (3H, d, *J* 11.2, N(CH_3)), 2.4–2.2 (2H, m, aliphatic), 2.0–1.9 (1H, m, aliphatic), 1.7–1.4 (3H, m, aliphatic), 1.2–0.7 (4H, m, aliphatic); δ_C (100 MHz, C_6D_6) 140.54 (C*i*, J_{P-C} 54.6), 133.82 (C*i*), 133.22 (C*i*), 130.65 (ArCH), 129.59 (ArCH), 126.29 (ArCH), 70.49 (CH, J_{P-C} 4.8), 65.62 (CH, J_{P-C} 5), 36.76 (CH_3, J_{P-C} 38.5), 32.18 (CH_3, J_{P-C} 12.8), 30.62 (CH_2), 28.8 (CH_2), 24.71 (CH_2), 24.42 (CH_2); δ_P (161 MHz, C_6D_6) 109.73 (Found: 326.0545. $C_{14}H_{20}Br^{79}N_2P$ requires M^+, 326.0547).

Synthesis of 2-methoxymethylphenylbis(dimethylamino)-phosphine

tert-Butyllithium (56.2 mL, 95.5 mmol) was added to a solution 2-methoxymethylbromobenzene (9.6 g, 48 mmol) in diethyl ether (200 mL) at −70 °C. After the addition was complete the temperature of the solution was maintained for 2 h. Meanwhile, hexamethylphosphorus triamide (5.78 mL, 31.83 mmol) was added dropwise to phosphorus trichloride (1.43 mL, 15.9 mmol) at 0 °C. The mixture was heated to 70 °C for 30 min to ensure complete redistribution to form bis(dimethylamino)-chlorophosphine; it was then cooled to −70 °C and the lithiate was added dropwise. The reaction mixture was allowed to warm up overnight and sodium bicarbonate (1 g) mixed with dichloromethane (4 mL) was added and stirred for 1 h. The solution was filtered under nitrogen to remove the inorganic salts and the solvent was removed by use of a high vacuum pump. The residue was distilled under vacuum to yield the product (bp 114 °C, 0.4 mmHg) (4.74 g, 41%) as a colourless oil. ν_{max}(thin film)/cm^{-1} 1427 (Ar–P), 1046 (P–N); δ_H (250 MHz, C_6D_6) 7.9 (1H, m, ArH), 7.6 (1H, m, ArH), 7.35–7.25 (2H, m, ArH), 4.64 (2H, s, C*H*2OCH$_3$), 3.28 (3H, s, OCH$_3$), 2.60 (12H, d, *J* 9, 2 × N$(CH_3)_2$); δ_C (62.8 MHz, C_6D_6) 141.53 (C*i*, J_{P-C} 18.7), 138.1 (C*i*, J_{P-C} 7.9), 130.7 (C*i*, J_{P-C} 5.9), 128.3 (ArCH), 127.2 (ArCH), 126.8 (ArCH), 72.4 (*C*H$_2$OMe, J_{P-C} 14.7), 58.14 (OCH$_3$), 41.35 (N$(CH_3)_2$, J_{P-C} 16.7); δ_P (161 MHz, C_6D_6) 96.5; *m*/*z* (EI) 240 (M^+, 8), 196 (60), 153 (50), 137 (80), 123 (30), 109 (20), 91 (50), 42 (100%) (Found: 240.1392. $C_{12}H_{21}N_2O_1P_1$ requires M^+, 240.1391).

Synthesis of (3a*R*,7a*R*)-1,3-dimethyl-2-(2-methoxymethylphenyl)-2,3,3a,4,5,6,7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 1h

(*R*,*R*)-*N*,*N*′-Dimethyl-1,2-diaminocyclohexane **2** (11.7 mg, 0.0826 mmol) was added to a solution of 2-methoxymethylphenylbis(dimethylamino)phosphine (20 mg, 0.083 mmol) in toluene (2 mL) at rt. The reaction mixture was stirred at reflux with a constant stream of nitrogen to allow the venting of dimethylamine as the reaction proceeded. After 1 day the outflow was non-basic, and the reaction mixture was allowed to cool. Removal of the toluene left **1h** (22 mg, 91%) as a viscous clear oil. $[\alpha]_D^{20}$ +46.36 (c = 1.1, $CHCl_3$); ν_{max}(thin film)/cm^{-1} 1446 (Ar–P), 1024 (P–N); δ_H (250 MHz, C_6D_6) 7.9 (1H, m ArH), 7.7 (1H, m, ArH), 7.35–7.25 (2H, m, ArH), 5.15 (1H, dd, *J* 2.5 and 12, C*H*OCH$_3$), 5.0 (1H, dd, *J* 2.5 and 12, C*H*OCH$_3$), 3.31 (3H, s, OCH$_3$), 2.69 (3H, d, *J* 15, N(CH_3)), 2.37 (3H, d, *J* 17, N(CH_3)), 2.6–2.0 (3H, m, aliphatic), 1.8–0.8 (7H, m, aliphatic); δ_C (100 MHz, C_6D_6) 143.0 (C*i*, J_{P-C} 20.8), 139.37 (C*i*, J_{P-C} 46.6), 131.3 (C*i*), 129.13 (ArCH), 128.2 (ArCH), 126.5 (ArCH), 71.9 (CH, J_{P-C} 22.5), 69.75 (*C*H$_2$OCH$_3$, J_{P-C} 4.8), 65.9 (CH, J_{P-C} 8), 58.2 (*C*H$_2$OCH$_3$), 37.31 (CH_3, J_{P-C} 36.9), 32.26 (CH_3, q, J_{P-C} 16), 30.66 (CH_2), 28.94 (CH_2), 24.76 (CH_2), 24.57 (CH_2); δ_P (161 MHz, C_6D_6) 110.4 (Found: 292.1708. $C_{14}H_{21}N_2P$ requires M^+, 292.1705).

Synthesis of dibenzofuran-2-ylbis(dimethylamino)phosphine

Dibenzofuran (2.0 g, 11.9 mmol) was dissolved in THF (10.0 mL) and cooled to −78 °C. *n*-BuLi (5.3 mL, 12.5 mmol of a 2.4 M solution in hexanes) was added dropwise. The mixture was then allowed to warm to rt and stirred for 3 h. In a separate vessel PCl_3 (0.34 mL, 3.9 mmol) was cooled to 0 °C and HMPT (1.4 mL, 7.9 mmol) was added slowly, dropwise. After the vigorous, fuming reaction had subsided the mixture was heated to 70 °C for 30 min. The colourless oil was allowed to cool to rt and diluted with THF (5.0 mL). The lithiated dibenzofuran was recooled to −78 °C and the solution of $ClP(NMe_2)_2$ added *via* cannula. The pale yellow solution was stirred at −78 °C for 2 h and then allowed to stir at rt overnight. The reaction was quenched by the addition of sodium bicarbonate solution and the aqueous phase extracted with ether (3 × 50 mL). The combined organic extracts were dried over potassium carbonate, filtered and the solvent evaporated to give an orange oil. A portion (0.5 g) of this oil was purified by flash chromatography on RP-18 silica eluted with 1% Et_3N–MeCN to give the product as a colourless oil (361 mg). ν_{max}(liquid film)/cm^{-1} 1448 (P–Ar), 1058 (P–N); δ_H (250 MHz, $CDCl_3$) 7.96–7.87 (2H, m, ArH), 7.58–7.32 (5H, m, ArH), 2.81 (12H, d, *J* 9.6, NMe); δ_C (60 MHz, $CDCl_3$) 156.5 (C*i*, Ar), 156.0 (C*i*, Ar), 130.0 (ArCH), 126.7 (ArCH), 124.4 (C*i*, Ar), 123.9 (C*i*, Ar), 122.5 (ArCH), 122.3 (ArCH), 120.2 (ArCH), 120.1 (ArCH), 111.5 (ArCH), 41.5 (CH_3); δ_P (160 MHz, $CDCl_3$) 92.45 (s); *m*/*z* (EI) 286 (M^+, 70%) (Found: 286.1235. $C_{16}H_{19}N_2OP$ requires M, 286.1235).

(3a*R*,7a*R*)-1,3-Dimethyl-2-(dibenzofuran-2-yl)-2,3,3a,4,5,6,-7,7a-octahydro-1*H*-1,3,2-benzodiazaphosphole 1i

Dibenzofuran-2-ylbis(dimethylamino)phosphine (108 mg, 0.37 mmol) was dissolved in toluene (2.0 mL). To this was added (*R*,*R*)-*N*,*N*′-dimethyl-1,2-diaminocyclohexane **2** (53 mg, 0.37 mmol) and the was mixture heated to reflux for 3 days. The solvent was then evaporated to give **1i** as a yellow oil (125 mg, 100%). $[\alpha]_D^{20}$ = +155.3 (c = 1.23, $CHCl_3$); ν_{max}(liquid film)/cm^{-1} 1464 (P–Ar), 1025 (P–N); δ_H (400 MHz, $CDCl_3$) 7.94–7.91 (2H, m, ArH), 7.66–7.61 (2H, m, ArH), 7.46–7.41 (1H, td, *J* 7.4, 1.4, ArH), 7.37–7.30 (1H, m, ArH), 7.24–7.22 (1H, m, ArH), 2.80

(3H, d, *J* 15.8, CH_3), 2.46–2.38 (1H, m, CH), 2.37 (3H, d, *J* 15.9, CH_3), 2.31–2.23 (2H, m, CH + $(CH_2)_4$), 1.93–1.76 (3H, m, $(CH_2)_4$), 1.40–1.14 (4H, m, $(CH_2)_4$); δ_C (100 MHz, $CDCl_3$) 156.0 (C*i*, Ar), 130.2 (ArCH, J_{P-C} 3.2), 128.9 (ArCH), 126.8 (ArCH), 125.2 (C*i*, Ar), 123.3 (C*i*, Ar), 122.5 (ArCH), 121.9 (C*i*, Ar), 121.3 (ArCH), 120.5 (ArCH), 111.7 (ArCH), 71.0 (CH, J_{P-C} 4.9), 66.2 (CH, J_{P-C} 9.6), 36.9 (CH_3), 30.8 (CH_3, J_{P-C} 8.1), 30.0 (CH_2), 28.6 (CH_2, J_{P-C} 3.2), 24.4 (CH_2), 24.0 (CH_2); δ_P (160 MHz, $CDCl_3$) 102.4 (s); *m/z* (FAB) 339 (MH^+, 52%) (Found: 338.1550. $C_{20}H_{23}N_2OP$ requires M^+, 338.1548).

Synthesis of bis(diazaphospholidine) 4

(*R*,*R*)-*N*,*N*′-Dimethyl-1,2-diaminocyclohexane **2** (126 mg, 0.886 mmol) was added to solution of **5** (141 mg, 0.443 mmol) in toluene (5 mL) at rt. The reaction mixture was stirred at reflux with a constant stream of nitrogen to allow the venting of dimethylamine as the reaction proceeded. After 3 days the outflow was non-basic, and the reaction mixture was allowed to cool. Removal of the toluene left **4** (185 mg, 100%) as a yellow solid. Mp 57–59 °C; $[\alpha]_D^{20}$ +7.75 (*c* = 0.4, $CHCl_3$); ν_{max}(solution in C_6D_6)/cm^{-1} 1449 (Ar–P), 1023 (P–N); δ_H (400 MHz, C_6D_6) 8.07 (2H, m, ArH), 7.38 (2H, dd, *J* 5 and 3, ArH), 2.72 (6H, t, *J* 7.7, 2 × CH_3), 2.68 (6H, t, *J* 7.7, 2 × CH_3), 2.58–2.48 (2H, m, CH), 2.45–2.35 (2H, m, CH), 2.1–2.02 (2H, m, CH), 1.81–1.74 (2H, m, $(CH_2)_4$), 1.7–1.5 (4H, m, $(CH_2)_4$), 1.4–1.25 (2H, m, $(CH_2)_4$), 1.2–0.9 (6H, m, $(CH_2)_4$); δ_C (62.8 MHz, C_6D_6) 145.6 (C*i*, J_{P-C} 13.3), 130.8 (ArCH, J_{P-C} 4), 128.2 (ArCH, d), 70.54 (2 × CH), 65.5 (2 × CH, J_{P-C} 4), 37.2 (2 × CH_3, J_{P-C} 20), 32.5 (2 × CH_3, J_{P-C} 12.4), 30.26 (2 × CH_2), 29.1 (2 × CH_2), 24.9 (2 × CH_2), 24.5 (2 × CH_2); δ_P (161 MHz, C_6D_6) 110.31.

Synthesis of bis(diazaphospholidine) (C_2-symmetric) borane complex 6

Borane–dimethyl sulfide (0.43 mL, 2 M in toluene, 0.86 mmol) was added to a solution of bisphosphine **4** (120 mg, 0.287 mmol) in THF (2 mL) at −40 °C. The reaction mixture was allowed to warm to rt and stirred overnight. After this period the reaction was quenched by the cautious addition of sodium hydrogen carbonate (5 mL), extracted with DCM (3 × 5 mL), dried over anhydrous magnesium sulfate, filtered and concentrated to leave a white solid. Purification by column chromatography on a silica gel column by elution with diethyl ether–hexane (1 : 9) yielded **6** as a white crystalline solid (117 mg, 91%). Mp 89–90 °C (Found: C, 58.99; H, 9.35; N, 12.4. $C_{22}H_{42}P_2N_4B_2$ requires C, 59.22; H, 9.48; N, 12.55%); $[\alpha]_D^{20}$ −14.2 (*c* = 0.5, $CHCl_3$); ν_{max}(solution in CH_2Cl_2)/cm^{-1} 1449 (Ar–P), 1050 (P–N); δ_H (250 MHz, $CDCl_3$) 7.6–7.4 (2H, m, ArH), 7.44–7.36 (2H, m, ArH), 2.93 (6H, d, *J* 9, 2 × CH_3), 2.64 (6H, d, *J* 17, 2 × CH_3), 2.68–2.6 (2H, m, CH), 2.35–2.2 (2H, m, CH), 2.2–2.1 (2H, m, $(CH_2)_4$), 1.8–1.65 (4H, m, $(CH_2)_4$), 1.5–1.4 (2H, m, $(CH_2)_4$), 1.35–1.05 (4H, m, $(CH_2)_4$), 1.0–0.8 (4H, m, $(CH_2)_4$); δ_C (62.8 MHz, $CDCl_3$) 139.5 (C*i*, J_{P-C} 10), 133.5 (ArCH, J_{P-C} 13), 129.37 (ArCH, J_{P-C} 10), 65.1 (2 × CH, J_{P-C} 2), 64.6 (2 × CH, J_{P-C} 4), 34.15 (2 × CH_3, J_{P-C} 7.6), 31.5 (2 × CH_3, J_{P-C} 3.8), 30.5 (2 × CH_2, J_{P-C} 4.3), 26.9 (2 × CH_2, J_{P-C} 5.2), 24.9 (2 × CH_2), 24.2 (2 × CH_2); δ_P (161 MHz, $CDCl_3$) 119. Recrystallisation from dichloromethane–hexane yielded an X-ray quality crystal.

Palladium-catalysed allylic alkylation with dimethyl malonate

Ligand **1c** (89 mg, 0.32 mmol) was dissolved in DCM (0.5 mL) and to this was added allylpalladium chloride dimer (14.6 mg, 0.040 mmol) as a solution in DCM (0.5 mL). The mixture was heated to 40 °C for 2 h then allowed to cool to rt. 1,3-Diphenyl-3-acetoxyprop-1-ene **7** (200 mg, 0.79 mmol) was then added as a solution in DCM (1.0 mL) followed by dimethyl malonate (115 mg, 0.87 mmol), BSA (176 mg, 0.87 mmol) and sodium acetate (1 mg). The resultant suspension was stirred at rt for 16 h before diluting with ether and quenching with ammonium chloride solution. The aqueous phase was extracted with ether (3 × 10 mL), the combined organics were dried over sodium sulfate, filtered and the solvent evaporated. Purification by flash chromatography on silica eluted with 10% ethyl acetate–petrol gave **8** as a colourless oil (294 mg, 97%). δ_H (250 MHz, $CDCl_3$) 7.33–7.19 (10H, m, ArH), 6.48 (1H, d, *J* 15.7, =CHPh), 6.31 (1H, dd, *J* 15.7, 8.1, =CH-), 4.26 (1H, dd, *J* 10.8, 8.1, CH), 3.95 (1H, d, *J* 11.0, C*H*$(CO_2Me)_2$), 3.70 (3H, s, CH_3), 3.52 (3H, s, CH_3). The observed data agree with literature values.[3a,b] The enantiomeric excess was determined to be 89% (*R*) by chiral shift NMR using (+)-Eu(hfc)$_3$. A sample of **8** of known mass (approx. 20 mg) was dissolved in $CDCl_3$ (1.0 mL). This solution was then added to a sample vial containing 4–4.5 equivalents of (+)-Eu(hfc)$_3$ and shaken for a few seconds until a bright yellow solution had formed. NMR analysis of this sample (250 MHz) gave 4 sharp signals in the region of 4.0 ppm. The ratio of signal 1 (4.24 ppm) and signal 2 (4.13 ppm) gave a measure of the enantioselectivity. Signal 1 was the major peak corresponding to the (*R*)-enantiomer in this system.[3b]

Palladium-catalysed allylic amination reactions with sodium toluene-*p*-sulfonamide

Toluene-*p*-sulfonamide (137 mg, 0.80 mmol) was added slowly to a suspension of sodium hydride (32 mg, 0.80 mmol) in THF (4.0 mL). The mixture was allowed to stir at rt for 2 h and then the solvent was removed under reduced pressure and the sodium salt resuspended in DCM (2.0 mL). In the meantime ligand **1c** (22.2 mg, 0.081 mmol) was dissolved in DCM (0.5 mL) and to this was added solid allylpalladium chloride dimer (7.3 mg, 0.021 mmol). The mixture was heated to 40 °C for 1.5 h and then allowed to cool to rt. 1,3-Diphenyl-3-acetoxyprop-1-ene **7** (100 mg, 0.42 mmol) was then added as a solution in DCM (0.5 mL degassed) followed by the suspension of toluene-*p*-sulfonamide sodium salt and sodium acetate (1 mg). The mixture was stirred at rt for 64 h and then quenched by the addition of ether and ammonium chloride solution. The aqueous phase was extracted with ether (3 × 10 mL) and the combined organics dried over sodium sulfate, filtered and solvent evaporated. Purification by flash chromatography on silica eluted with 15% ethyl acetate–petrol gave **9d** as a white solid (65 mg, 45%). $[\alpha]_D^{20}$ = +26.5 (*c* = 0.8, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 7.65 (2H, d, *J* 8.4, ArH), 7.26–7.13 (12H, m, ArH), 6.36 (1H, d, *J* 16.0, =CHPh), 6.07 (1H, dd, *J* 15.7, 6.7, =CH-), 5.11 (1H, t, *J* 7.0, CH), 4.89 (1H, d, *J* 7.3, NH), 2.32 (3H, s, CH_3). Agrees with literature values.[18] The enantiomeric excess was determined by chiral HPLC using a Chiralcel OD column, 75 : 25 hexane–propan-2-ol, 0.5 mL min^{-1}, 254 nm; ee = 75.6% (*S*), (+)-(*S*)-isomer t_r = 22.49 min, (−)-(*R*)-isomer t_r = 15.94 min.

The following were prepared according to the procedure described for *N*-(1,3-diphenylprop-2-enyl)toluene-*p*-sulfonamide **9d**.

***N*-(1,3-Diphenylprop-2-enyl)benzylamine 9a.**[17,18] Amine **9a** was formed as a colourless oil in 68% yield. $[\alpha]_D^{20}$ = +27.4 (*c* = 1.5, $CHCl_3$); δ_H (250 MHz, $CDCl_3$) 7.45–7.19 (15H, m, ArH), 6.58 (1H, d, *J* 15.7, =CHPh), 6.31 (1H, dd, *J* 16.0, 7.6, =CH-), 4.39 (1H, d, *J* 7.3, CH), 3.77 (2H, d, *J* 1.5, CH_2), 2.0 (1H, bs, NH). The enantiomeric excess was determined by chiral HPLC using a Chiralcel OD column, 200 : 1 hexane–propan-2-ol, 0.5 mL min^{-1}, 254 nm, ee = 78.1% (*S*), (+)-(*S*)-isomer t_r = 36.58 min, (−)-(*R*)-isomer t_r = 34.37 min.

(+)-(*S*)-*N*-(1,3-Diphenylprop-2-enyl)-(*R*)-α-methylbenzylamine 9b.[19] Amine **9b** was formed as a colourless oil in 67% yield as a mixture of diastereomers. $[\alpha]_D^{20}$ = +78.3 (*c* = 1.0, $CHCl_3$); ν_{max}($CHCl_3$ film)/cm^{-1} 3423 (NH), 1637 (C=C); δ_H (250 MHz, $CDCl_3$) 7.40–7.21 (15H, m, ArH), 6.41 (1H, d, *J* 16.0, = CHPh), 6.24 (1H, dd, *J* 16.0, 7.9, =CH-), 4.16 (1H, d, *J* 7.9,

CH), 3.90 (1H, q, *J* 6.7, C*H*MePh), 1.75 (1H, bs, NH), 1.39 (3H, d, *J* 6.7, CH_3); δ_C (60 MHz, $CDCl_3$) 145.5 (C*i*, Ar), 143.2 (C*i*, Ar), 136.9 (C*i*, Ar), 131.9 (CH, Ar), 130.9 (CH, Ar), 128.4 (CH, Ar), 127.3 (CH, Ar), 127.0 (CH, Ar), 126.8 (CH, Ar), 126.6 (CH), 126.3 (CH), 61.9 (CH), 54.9 (CH), 24.4 (CH_3).

(−)-(*S*)-*N*-(1,3-Diphenylprop-2-enyl)-(*S*)-α-methylbenzylamine 9c.[19] $[\alpha]_D^{20}$ = +8.5 (*c* = 1.45, $CHCl_3$); ν_{max}($CHCl_3$ film)/cm^{-1} 3422 (NH), 1654 (C=C); δ_H (250 MHz, $CDCl_3$) 7.33–7.24 (15H, m, ArH), 6.45 (1H, d, *J* 16.0, =CHPh), 6.26 (1H, dd, *J* 16.0, 7.8, =CH-), 4.17 (1H, d, *J* 7.8, CH), 3.65 (1H, q, *J* 6.7, C*H*MePh), 1.73 (1H, bs, NH), 1.33 (3H, d, *J* 6.7, CH_3); δ_C (60 MHz, $CDCl_3$) 145.5 (C*i*, Ar), 142.8 (C*i*, Ar), 136.9 (C*i*, Ar), 133.1 (CH, Ar), 129.4 (CH, Ar), 128.5 (CH, Ar), 128.4 (CH, Ar), 128.3 (CH, Ar), 127.5 (CH, Ar), 127.2 (CH, Ar), 127.0 (CH, Ar), 126.8 (CH, Ar), 126.6 (CH), 126.3 (CH), 62.1 (CH), 54.7 (CH), 24.5 (CH_3).

(+)-(*S*)-*N*-(1,3-Diphenylprop-2-enyl)pyrrolidine 9e. Amine **9e** was formed as a pale cream solid in 48% yield. $[\alpha]_D^{20}$ = +2.9 (*c* = 1.0, $CHCl_3$); ν_{max}($CHCl_3$ film)/cm^{-1} 2967, 2791, 1492, 1451, 1135, 965; δ_H (250 MHz, $CDCl_3$) 7.44–7.18 (10H, m, ArH), 6.56 (1H, d, *J* 15.7, =CHPh), 6.41 (1H, dd, *J* 15.7, 8.1, =CH-), 3.76 (1H, d, *J* 8.4, CH), 2.58–2.41 (4H, m, CH_2), 1.80–1.75 (4H, m, CH_2); δ_C (100 MHz, $CDCl_3$) 143.0 (C*i*), 136.9 (C*i*), 133.0 (CH), 129.7 (CH), 128.5 (CH), 128.3 (CH), 127.5 (CH), 127.2 (CH), 127.0 (CH), 126.3 (CH), 74.3 (CH), 53.0 (CH_2), 23.2 (CH_2); *m*/*z* (EI) 263 (M^+, 40%) (Found: 263.1674. $C_{19}H_{21}N$ requires *M*, 263.1674); HPLC (Chiralcel OD, 200 : 1 hexane–propan-2-ol, 0.5 mL min^{-1}, 254 nm) ee = 67.8% (*S*), (+)-(*S*)-isomer t_r = 11.72 min, (−)-(*R*)-isomer t_r = 10.49 min.

(+)-(*S*)-*N*-(1,3-Diphenylprop-2-enyl)-*N*′-benzylpiperazine 9f. Amine **9f** was formed as a white solid in 63% yield. $[\alpha]_D^{20}$ = +15.4 (*c* = 1.0, $CHCl_3$); ν_{max}($CHCl_3$ film)/cm^{-1} 2938, 2813, 1637, 1494, 1452, 1136, 1004, 967; δ_H (250 MHz, $CDCl_3$) 7.40–7.18 (15H, m, ArH), 6.54 (1H, d, *J* 15.7, =CHPh), 6.30 (1H, dd, *J* 16.0, 8.7, =CH-), 3.81 (1H, d, *J* 8.7, CH), 3.51 (2H, s, CH_2), 2.46 (8H, m, CH_2); δ_C (100 MHz, $CDCl_3$) 141.7 (C*i*), 137.8 (C*i*), 136.7 (C*i*), 131.5 (CH), 131.0 (CH), 129.0 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.9 (CH), 127.3 (CH), 127.0 (CH), 126.8 (CH), 126.2 (CH), 74.1 (CH), 62.9 (CH_2), 53.0 (CH_2), 51.3 (CH_2); *m*/*z* (CI) 369 (MH^+, 15%) (Found: 369.2331 $C_{26}H_{28}N_2$ requires MH, 369.23307); HPLC (Chiralcel OD, 200 : 1 hexane–propan-2-ol, 0.4 mL min^{-1}, 254 nm) ee = 58.3% (*S*), (+)-(*S*)-isomer t_r = 25.70 min, (−)-(*R*)-isomer t_r = 28.05 min.

Crystal data for 3

$C_{15}H_{26}BN_2OP$, *M* = 292.16, orthorhombic, space group $P2_12_12_1$, *a* = 8.300(4), *b* = 13.789(5), *c* = 14.553(5) Å, *U* = 1665.6(11) $Å^3$, *T* = 200(2) K, *Z* = 4, D_{calc} = 1.165 Mg m^{-3}, *F*(000) = 632, μ(Mo-Kα) = 0.163 mm^{-1}. Crystal character: colourless blocks. Crystal dimensions 0.2 × 0.2 × 0.16 mm, 7586 reflections measured, 2605 unique [*R*(int) = 0.0852]. *R*1[for 1846 reflections with $I > 2\sigma(I)$] = 0.0637, *wR*2 (all data) = 0.1124. 193 parameters. Absolute structure parameter *x* = 0.23(19).

Crystal data for 6

$C_{22}H_{42}B_2N_4P_2$, *M* = 446.16, orthorhombic, space group $P2_12_12_1$, *a* = 13.347(2), *b* = 13.738(2), *c* = 14.152(2) Å, *U* = 2595.04(13) $Å^3$, *T* = 180(2) K, *Z* = 4, D_{calc} = 1.142 Mg m^{-3}, *F*(000) = 968, μ(Mo-Kα) = 0.184 mm^{-1}. Crystal character: colourless blocks. Crystal dimensions 0.4 × 0.4 × 0.2 mm, 15612 reflections measured, 6068 unique [*R*(int) = 0.0433]. *R*1[for 4736 reflections with $I > 2\sigma(I)$] = 0.0493, *wR*2 (all data) = 0.1044. 277 parameters. Absolute structure parameter *x* = −0.02(8).

CCDC reference numbers 169156 and 169157. See http://www.rsc.org/suppdata/p1/b1/b106399p/ for crystallographic files in .cif or other electronic format.

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