Directed *ortho* Metallation Chemistry and Phosphine Synthesis: New Ligands for the Suzuki–Miyaura Reaction

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Abstract: We describe the use of the phosphinic amide moiety as an effective directed *ortho* metallation group for the incorporation of various phosphino groups onto a benzene ring to generate phosphine ligands. These ligands were used to generate active palladium catalysts for the Suzuki–Miyaura reaction in which deactivated aryl bromides and some aryl chlorides were used as substrates. Surprisingly and interestingly, the (2-alkylphenyl)phosphine derivatives were found to be especially active. The stereoelectronic and electronic features of the ligands were probed by use of selenium oxidation products and Vaska's rhodium complexes, respectively. Some unusual features were observed, specifically relating to the inductive effects of the alkyl side chains in relation to the electron-withdrawing phosphinic amide functions. The two probes were also compared, and the results were related to the catalytic data obtained from the Suzuki reactions. Quite unexpectedly, the ligands generate catalysts with good activity despite their being relatively electron-poor. This low electron density, resulting from the phosphinic amide functionality, renders them stable to oxidation and hydrolysis for over six months while exposed to air. Additionally, the use of the phosphinic amide directing group is unusual and rare, and has not, to our knowledge, been noted before in the preparation of phosphine ligands.

Key words: C–C bond formation, directed *ortho* metallation, ligand effects, palladium, Suzuki–Miyaura cross-coupling

Ligands are key features of transition-metal catalysts, modifying their activity and selectivity. In C–C bond-formation reactions, the Suzuki–Miyaura reaction,[1] a central reaction type in organic chemistry, has become one of the most important tools. Recent ligand developments allow the use of aryl chloride substrates and low catalyst loadings at temperatures between ambient and 110 °C.[1] Hindered electron-rich ligands are thought to enhance the rate of oxidative addition,[1d–f] although preference for the coordinatively unsaturated highly reactive L_1Pd species may be causative.[1f] While electron-rich ligands are susceptible to oxidation, protection and in situ deprotection approaches are known (but involve additional steps or reagents).[2] Ligandless methods for effecting Suzuki–Miyaura reactions with aryl bromides are known,[3a] and secondary phosphine oxides[3b] have been used as preligands in attempts to circumvent some of the problems associated with more electron-rich systems. The use of N-heterocyclic carbenes as ligands eliminates the oxidation problems associated with electron-rich phosphines, but typically requires higher catalyst loadings and reaction temperatures than with phosphines,[4] although very recent work has improved on those shortcomings.[4b] Phosphites are also useful in this context,[5] but tend to be hydrolytically sensitive.

Directed *ortho* metallation (DoM)[6] has been used in a great many syntheses and has been shown to be one of the most powerful methods with which to selectively functionalise aromatic systems.

We herein report an expedient rapid synthesis of ligands derived from phosphinic amide that have been found to be suitable for the Suzuki–Miyaura reaction at low palladium catalyst loadings. The brief practical synthesis affords triarylphosphine ligands resistant to oxidation and hydrolysis while maintaining high catalyst activity. The synthesis rests strongly on DoM,[6] making use of a directing group that is highly underrepresented in this type of chemistry. Phosphonic amides have previously seen limited use as the directing group in DoM reactions,[7] but have been considered poor DoM groups with regard to their further application, while phosphinic amides have been used for double *ortho* lithiation reactions[8a] and, recently,[8b] also in the context of desymmetrisation chemistry. We have been working in this area for some time,[8c–e] and are prompted by recent interest in this field to publish our results. We envisioned that the use of phosphinic amides as directing groups, together with phosphinous chloride (R_2PCl) electrophiles, would allow the synthesis of sterically hindered phosphines that are stable to hydrolysis and oxidation.

Phosphinic amides **1** were prepared in high yields in a simple two-step one-pot reaction from cheap, readily available starting materials (Scheme 1). The *ortho* deprotonation of compounds **1** with *sec*-butyllithium and quenching with diphenylphosphinous chloride (Ph_2PCl) or dicyclohexylphosphinous chloride (Cy_2PCl) allowed isolation of the desired products **2** (45–60% yield), which are stable to air, liquid–liquid extraction, and chromatography without special exclusion of oxygen. Aniline derivative **2k** (Figures 1, 73% yield) was similarly prepared from bis[4-(dimethylamino)phenyl]phosphinous chloride [$(4\text{-}Me_2NC_6H_4)_2PCl$]. If the electrophile (P–Cl compound) was added to the nucleophile (lithiated material), mixtures of the monosubstituted products **2** shown in Scheme 1 and the disubstituted analogues, in which each phenyl ring possesses PPh_2 substitution, were obtained. To circumvent this problem, a reverse mode of addition was followed, namely the addition of the electrophile to the nucleophile. In this way an excess of the electrophile

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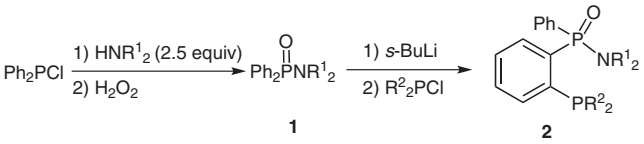
was maintained and the reaction became selective for the products shown in Scheme 1.



1a (R^1 = Et, 95%), **1b** (R^1 = *i*-Pr, 93%), **1c** (R^1 = *i*-Bu, 96%),
2a (R^1 = Et, R^2 = Ph, 58%), **2b** (R^1 = *i*-Pr, R^2 = Ph, 56%),
2c (R^1 = *i*-Bu, R^2 = Ph, 47%), **2d** (R^1 = Et, R^2 = Cy, 45%),
2e (R^1 = *i*-Pr, R^2 = Cy, 51%), **2f** (R^1 = *i*-Bu, R^2 = Cy, 43%),
2g (R^1 = Et, R^2 = 2-Tol, 48%), **2h** (R^1 = *i*-Pr, R^2 = 2-Tol, 48%),
2i (R^1 = Et, R^2 = 2-EtC_6H_4, 62%), **2j** (R^1 = Et, R^2 = 2-xylyl, 58%)

Scheme 1 General ligand synthesis approach

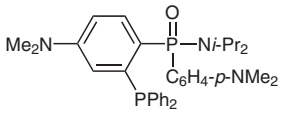


Figure 1 Ligand **2k**

The electronic characteristics of a selected subset of the ligands were investigated (Table 1) using probes that are sensitive (a) exclusively to the electron density at the phosphorus(III) atom (employing the IR CO stretching frequency in the corresponding rhodium Vaska complexes)[9] or (b) to stereoelectronic effects (specifically the s character of the phosphorus atom, which is also influenced by steric effects), making use of P–Se coupling constants calculated from the ^{31}P NMR spectra of the ligands after their oxidation with elemental selenium.[10]

The IR absorptions of the Vaska rhodium complexes (Table 1) placed the σ-donor ability of the first three ligands in the order **2b** > **2c** > **2a**. These electronic changes in the phosphorus(III) atom arise exclusively by virtue of changing the alkyl groups contained in the remote phosphinic amide function and originate from inductive effects.[11] Importantly (as a backdrop to the catalytic data, *vide infra*), ligands **2a–c** were more electron-deficient than triphenylphosphine, as was anticipated and seen in Table 1, and were electronically similar to (pentafluorophenyl)diphenylphosphine [$PPh_2(C_6F_5)$] or tris(4-fluorophenyl)phosphine [$P(4\text{-}FC_6H_5)_3$].[9] Somewhat astonishingly, the 2-tolyl analogues **2g** and **2h** were more electron-rich than triphenylphosphine, despite the presence of the electron-withdrawing P(O)N group. The inductive effect of the methyl groups in the latter instances is greater than the electron-withdrawing effects of the P(O)N group (compare IR stretching frequencies of **2a**/**2g** or **2b**/**2h** vs PPh_3), pointing to a significant electronic influence of those alkyl functions. The positive inductive effect of the ethyl group over the methyl (Me, **2g** vs Et, **2i**) evidently also enhances the electron density on the phosphorus atom.

Table 1 Stereoelectronic Characteristics of Ligands **2**

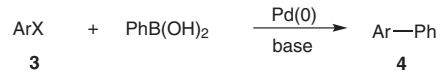
Ligand	ν(Rh–CO) (cm^{-1})[a]	$^1J(^{31}P–^{77}Se)$ (Hz)
2a	1984	722.5
2b	1982	718.3
2c	1983	716.4
PPh_3	1979 (1979)[b]	732.0
2d	1971	687.4
2e	1970	685.2
2f	1970	684.9
2g	1970	723.6
2h	1966	714.3
2i	1962	697.3
2j	1965	682.0
2k	1970	–[c]

[a] The IR spectra were obtained for the *trans*-[$RhCl(CO)L_2$] complexes in solution ($CHCl_3$).
[b] The solution-phase value ($CHCl_3$) reported in the literature is given in parentheses; see ref. 9.
[c] The coupling constant was not determined.

The combined stereoelectronic effect of the alkyl R^1 group in ligands **2a–c** can be observed in the P–Se coupling constants for these compounds (Table 1). These data confirm that the phosphorus atoms of these ligands have greater s character than triphenylphosphine (smaller P–Se coupling constants). Within this series, the effect of the steric influence of the alkyl group is also evident. The steric bulk of the isobutyl group is more removed from the phosphorus(V) atom, and it consequently impinges more on the remote phosphorus(III) atom than would the isopropyl group. This accounts for the stereoelectronic series providing s character in the order **2c** > **2b** > **2a** afforded by this probe, which is slightly different from that elucidated by the series determined for the Vaska-type complex (purely electronic).

The ligands readily promote the palladium-mediated Suzuki–Miyaura reaction (Scheme 2) when strongly deactivated aryl bromides and some aryl chlorides are used. Both of these substrates are resistant to the oxidative addition step that initiates the catalytic cycle.[12] Initial reactions using one mol% palladium(II) acetate and ligand **2a** were performed in tetrahydrofuran, providing the biaryl products **4a** (93%), **4b** (89%), **4c** (38%) and **4d** (11%), respectively.

Clearly, ligands **2a** performed very well in the reactions of deactivated aryl bromide substrates **3a** and **3b** but relatively poorly for aryl chlorides **3c** and **3d** (Scheme 2). The reaction already showed significant promise and scope for improvement when use is made of a combination of reaction conditions and improvements to the ligand itself. Solvent, base, additives, temperature, and reaction time are



3a: Ar = 4-$MeOC_6H_4$ X = Br
3b: Ar = 4-$Me_2NC_6H_4$ X = Br
3c: Ar = 4-NCC_6H_4 X = Cl
3d: Ar = 2-pyridyl X = Cl

4a: Ar = 4-$MeOC_6H_4$
4b: Ar = 4-$Me_2NC_6H_4$
4c: Ar = 4-NCC_6H_4
4d: Ar = 2-pyridyl

Scheme 2 Substrates and products from Suzuki–Miyaura reactions

known to have profound effects on catalyst activity,[1b] and the reactions were consequently optimised for solvent (THF, toluene, DME, DMF), base (K_3PO_4, K_2CO_3, *t*-BuOK), precatalyst [$Pd(OAc)_2$, $Pd_2(dba)_3$], catalyst concentration (0.1, 0.05, 0.01 mol%), and reaction temperature (60 °C, 100 °C). Reactions performed in toluene with 0.1 mol% of palladium(II) acetate and either potassium carbonate or potassium phosphate as the base were optimum. Subsequent reactions of several strongly deactivated aryl bromides (Table 2) and activated aryl chlorides (Table 3) were carried out under these conditions. Here, ligands with substituent manipulations as contained in Scheme 1 were put to the test.

Table 2 Suzuki–Miyaura Reaction: Aryl Bromide Substrates[a]

Amount $Pd(OAc)_2$ (mol%)	Pd/L ratio	Temp (°C)	Ligand	Yield **4a** (%)[b]	Yield **4b** (%)[b]
0.1	1:2	60	**2a**	88	84
0.05	1:2	60	**2a**	92 (89)[c]	82
0.05	1:2	100	**2a**	81	77
0.01	1:1	100	**2a**	83	68
0.1	1:2	60	**2b**	81	79
0.01	1:2	60	**2b**	77	67
0.1	1:2	60	**2c**	95 (93)[c]	65
0.1	1:1	100	**2d**	–[d]	64
0.1	1:1	100	**2e**	–[d]	87
0.1	1:1	100	**2f**	–[d]	68
0.1	1:2	100	**2k**	–[d]	89

[a] Reaction conditions: $Pd(OAc)_2$, $PhB(OH)_2$ (1.5 equiv), toluene, K_3PO_4 (2.0 equiv), 24 h.
[b] Yields based on GC-FID analysis.
[c] The yields in parentheses are isolated yields, the average of three runs.
[d] Reaction not performed.

The size of the alkyl group attached to the amine played a significant role in the activity of the palladium catalyst formed from the various ligands, the activity order being *i*-Pr > *i*-Bu > Et as a rule, as anticipated from the IR information shown in Table 1 and also as pre-empted on the basis of literature precedent indicating that bulkier ligands improve catalyst activity in such reactions.[2c,13] An increase in yield for the cyclohexylphosphine ligands (**2d** and **2f**) was observed and attributed primarily to the more electron-rich nature of the ligand, but also to the increased steric crowding. In these two specific instances, a 2:1 ligand/palladium ratio produced very poor reactions, while a 1:1 ratio afforded highly active catalysts and was critical to a successful outcome, in accordance with previous observations.[3] These ligands may well be hemi-labile chelators in solution, by analogy with P,P(O) systems.[14] The phosphinic amide group therefore plays two roles, namely as a DoM group and to bind to the palladium centre during catalysis. Most interestingly, the *ortho*-substituted ligands (**2g**–**j**) were particularly active towards the aryl chloride substrates. This development is unusual and provides unique instances in which a relatively electron-deficient triarylphosphine ligand formed active palladium catalysts for Suzuki–Miyaura coupling reactions for such substrates. An advantage of catalysts prepared from the ethylphenyl- and xylyl-substituted ligands is their ability to catalyse the reaction in question at 60 °C without forgoing catalyst activity. Importantly, the ligands of this study were stable for over six months while open to the atmosphere, neither losing any activity nor being oxidised or hydrolysed during that period. This particular aspect implies ready handling in air without fear of ligand degradation and is particularly attractive if special equipment or reactors are unavailable or where high ligand stability is desirable. Since the ligands of this study are chiral entities (P-chiral at the phosphinic amide moiety), albeit in a racemic form, these ligands lend themselves to asymmetric catalysis. In principle, it is possible to generate products identical to those detailed here but in an enantiomerically

Table 3 Suzuki–Miyaura Reaction: Aryl Chloride Substrates[a]

Pd/L ratio	Temp (°C)	Ligand	Yield **4c** (%)[b]	Yield **4d** (%)[b]
1:2	60	**2a**	19	35
1:2	60	**2b**	36	59
1:2	60	**2c**	37	54
1:1	60	**2d**	96 (93)[c]	80
1:1	100	**2e**	76	88
1:1	100	**2f**	75	87
1:2	100	**2g**	96 (92)[c]	79
1:1	100	**2h**	92	84
1:1	60	**2i**	85	77 (73)[c]
1:1	60	**2j**	86	72 (71)[c]
1:1	60	**2k**	74	63
1:2	100	**2k**	71	74

[a] Reaction conditions: $Pd(OAc)_2$ (0.1 mol%), $PhB(OH)_2$ (1.5 equiv), toluene, K_2CO_3 (2.0 equiv), 24 h.
[b] Yields based on GC-FID analysis.
[c] The yields in parentheses are isolated yields, the average of three runs.

pure form, by inducing chirality at the DoM stage of the reaction. Additionally, these ligands promise further potential by the fact that chiral phosphinic amides may be prepared from chiral amines, further enhancing the scope of potential application. These aspects are currently enjoying our attention.

In summary, the ease of synthesis of the novel ligands described here has allowed the preparation of a range of compounds stable to hydrolysis and oxidation, leading to desirably robust catalyst systems. The phosphinic amide functional group is shown to be an excellent DoM group with which to incorporate phosphorus-based electrophiles into the parent system. Our ligands have been shown to produce active palladium catalysts for the Suzuki–Miyaura reaction of activated aryl chlorides and strongly deactivated aryl bromides at low catalyst loadings (0.1 mol% for chlorides and 0.01 mol% for bromides) and modest temperatures. These results are being used in our laboratories to further refine the ligands and catalyst systems, with the view to improving their activity to include non-activated aryl chloride substrates.

All reactions were performed under an atmosphere of anhyd N_2. NMR spectra of samples in $CDCl_3$ (unless otherwise indicated) were recorded on a 300-MHz Varian Gemini 2000 spectrometer. Phosphorus- and proton-decoupled ^{13}C NMR spectra were measured (triple resonance probe) in many instances where two phosphorus atoms were present, to assist with individual peak identification. GC was carried out on a Varian Spectrum 3400 CX gas chromatograph using N_2 as the carrier gas with a split flow pressure of 1 atm. A DB1 30-m column was used that separated on the basis of boiling points. EI-MS was performed on a Thermo DFS spectrometer at an ionisation potential of 70 eV. IR spectroscopy was conducted on a Tensor 27 spectrometer; $CHCl_3$ was used as solvent.

Phosphinic Amides 1; General Procedure

The appropriate amine HNR^1_2 (0.225 mol, 2.5 equiv) was added to a soln of Ph_2PCl (16.3 mL, 0.09 mol) in toluene (250 mL) at 0 °C. The mixture was allowed to stir for 8 h at r.t., after which it was cooled to 0 °C and 30% H_2O_2 (15 mL) was added over 20 min. The mixture was allowed to stir for a further 1 h. The product was extracted with EtOAc (200 mL) and H_2O (3 × 50 mL) and the solvent was removed in vacuo. The product was isolated by flash column chromatography (silica gel, EtOAc).

***N*,*N*-Diethyl-*P*,*P*-diphenylphosphinic Amide (1a)**

Compound **1a** was synthesised from Et_2NH (23.4 mL, 0.225 mol, 2.5 equiv).

Yield: 95%; white powder; mp 135–138 °C; R_f = 0.25 (EtOAc).

IR ($CHCl_3$): 2976, 1173 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.81–7.75 (m, 4 H), 7.38–7.35 (m, 6 H), 3.00 (dq, *J* = 10.5, 7.2 Hz, 4 H), 1.03 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.3 (d, *J* = 127.9 Hz, 2 C), 132.2 (d, *J* = 9.2 Hz, 4 C), 131.9 (d, *J* = 2.8 Hz, 2 C), 128.2 (d, *J* = 12.3 Hz, 4 C), 39.2 (d, *J* = 3.5 Hz, 2 C), 14.0 (d, *J* = 3.8 Hz, 2 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 30.1 (s, 1 P).

MS (EI, 70 eV): *m*/*z* (%) = 274 (100) $[M]^+$.

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{16}H_{20}NOP$: 273.1283; found: 273.1281.

***N*,*N*-Diisopropyl-*P*,*P*-diphenylphosphinic Amide (1b)[8b]**

Compound **1b** was synthesised from *i*-Pr_2NH (31.7 mL, 0.225 mol, 2.5 equiv).

Yield: 93%; white powder; mp 130–133 °C; R_f = 0.30 (EtOAc).

IR ($CHCl_3$): 2977, 1173 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.77–7.71 (m, 4 H), 7.36–7.27 (m, 6 H), 3.38–3.30 (m, 2 H), 1.12 (d, *J* = 6.9 Hz, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.2 (d, *J* = 124.0 Hz, 2 C), 131.8 (d, *J* = 9.5 Hz, 4 C), 130.9 (d, *J* = 2.6 Hz, 2 C), 127.8 (d, *J* = 12.4 Hz, 4 C), 46.8 (d, *J* = 4.3 Hz, 2 C), 22.8 (d, *J* = 2.3 Hz, 4 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 30.1 (s, 1 P).

MS (EI, 70 eV): *m*/*z* (%) = 302 (100) $[M]^+$.

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{18}H_{24}NOP$: 301.1596; found: 301.1607.

***N*,*N*-Diisobutyl-*P*,*P*-diphenylphosphinic Amide (1c)**

Compound **1c** was synthesised from *i*-Bu_2NH (39.3 mL, 0.225 mol, 2.5 equiv).

Yield: 96%; white powder; mp 109.0–112.0 °C; R_f = 0.25 (hexanes–EtOAc, 1:1).

IR ($CHCl_3$): 2975, 1172 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.87–7.80 (m, 4 H), 7.44–7.35 (m, 6 H), 2.77 (dd, *J* = 7.2, 6.8 Hz, 4 H), 1.84 (m, 2 H), 0.78 (d, *J* = 6.6 Hz, 12 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.6 (d, *J* = 9.1 Hz, 4 C), 132.5 (d, *J* = 130.0 Hz, 2 C), 131.4 (d, *J* = 2.6 Hz, 2 C), 128.2 (d, *J* = 12.6 Hz, 4 C), 53.2 (d, *J* = 2.5 Hz, 2 C), 26.1 (d, *J* = 3.5 Hz, 2 C), 20.5 (s, 4 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 30.7 (s, 1 P).

MS (EI, 70 eV): *m*/*z* (%) = 330 (100) $[M^+]$.

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{20}H_{28}NOP$: 329.1909; found: 329.1918.

Phosphinic Amides 2; General Procedure

The appropriate phosphinic amide **1** (1.1 mmol) was weighed into a Schlenk flask and dissolved in THF (10 mL). The soln was cooled to –60 °C and 1 M *s*-BuLi in cyclohexane (1.1 equiv) was added. The soln was allowed to stir for 3 h at –40 to –70 °C. The soln was then cooled to –78 °C and added to the R^2_2PCl electrophile (1.2 equiv) dissolved in THF (10 mL). The reaction mixture was then allowed to warm to r.t. over 4 h and subsequently stirred at r.t. overnight. All solvents were then removed in vacuo and the residue was extracted with EtOAc (50 mL) and H_2O (3 × 10 mL). The product was purified by flash column chromatography (silica gel).

***P*-[2-(Diphenylphosphino)phenyl]-*N*,*N*-diethyl-*P*-phenylphosphinic Amide (2a)**

Compound **2a** was synthesised from **1a** (300 mg, 1.10 mmol) and Ph_2PCl (237 μL, 1.32 mmol) as the electrophile. Addition of the anion soln to a soln of the electrophile Ph_2PCl in THF (10 mL) was carried out to increase the yield of the product.

Yield: 58%; white foam; R_f = 0.13 (hexanes–EtOAc, 2:1).

IR ($CHCl_3$): 3011, 2402, 1217, 667 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.83 (m, 1 H), 7.61 (ddd, *J* = 12.0, 6.9, 1.5 Hz, 2 H), 7.40–7.04 (m, 16 H), 3.13–3.01 (m, 4 H), 1.04 (d, *J* = 7.2 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0 (dd, *J* = 26.1, 12.6 Hz, 1 C), 137.3 (dd, *J* = 125.2, 28.8 Hz, 1 C), 137.9 (2 × d, *J* = 37.4 Hz, 2 C), 136.0 (d, *J* = 12.4 Hz, 1 C), 133.5 (d, *J* = 10.4 Hz, 2 C), 133.2 (d, *J* = 9.8 Hz, 2 C), 133.4 (d, *J* = 10.3 Hz, 1 C), 133.2 (d, *J* = 126.4 Hz,

1 C), 131.9 (d, *J* = 9.8 Hz, 1 C), 131.8 (d, *J* = 9.5 Hz, 1 C), 130.9 (d, *J* = 2.6 Hz, 1 C), 130.7 (d, *J* = 2.6 Hz, 2 C), 127.9–127.5 (m, 9 C), 39.3 (d, *J* = 3.2 Hz, 2 C), 13.8 (d, *J* = 2.7 Hz, 2 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.8 (d, *J* = 3.3 Hz, 1 P), –10.5 (d, *J* = 3.3 Hz, 1 P).

MS (CI): *m*/*z* (%) = 458 (55) $[M + H]^+$, 385 (100).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{28}H_{29}NOP_2$: 457.1724; found: 457.1701.

_P_-[2-(Diphenylphosphino)phenyl]-_N_,_N_-diisopropyl-_P_-phenylphosphinic Amide (2b)

Compound **2b** was synthesised from **1b** (300 mg, 1.00 mmol) and Ph_2PCl (215 μL, 1.20 mmol). Addition of the anion soln to a soln of the electrophile Ph_2PCl in THF (10 mL) was carried out to increase the yield of the product.

Yield: 56%; white foam; R_f = 0.27 (hexanes–EtOAc, 2:1).

IR ($CHCl_3$): 3015, 2400, 1200, 667 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.92 (m, 1 H), 7.60–7.52 (m, 2 H), 7.39–7.01 (m, 16 H), 3.41 (sept, *J* = 6.9 Hz, 2 H), 1.30 (d, *J* = 6.9 Hz, 6 H), 1.14 (d, *J* = 6.6 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0 (dd, *J* = 26.8, 13.1 Hz, 1 C), 139.6 (dd, *J* = 124.7, 28.4 Hz, 1 C), 138.3 (dd, *J* = 87.0, 15.0 Hz, 2 C), 136.5 (d, *J* = 13.3 Hz, 1 C), 135.7 (dd, *J* = 121.8, 1.5 Hz, 1 C), 133.5 (d, *J* = 19.0 Hz, 2 C), 133.3 (d, *J* = 18.2 Hz, 2 C), 132.7 (dd, *J* = 10.6, 7.0 Hz, 1 C), 131.7 (d, *J* = 9.9 Hz, 1 C), 131.7 (d, *J* = 9.8 Hz, 1 C), 130.7 (d, *J* = 7.7 Hz, 1 C), 130.4 (d, *J* = 2.7 Hz, 1 C), 127.8–127.4 (m, 9 C), 46.8 (d, *J* = 4.3 Hz, 2 C), 22.8 (d, *J* = 2.3 Hz, 4 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.1 (d, *J* = 6.2 Hz, 1 P), –11.0 (d, *J* = 6.2 Hz, 1 P).

MS (CI): *m*/*z* (%) = 486 (50) $[M + H]^+$, 385 (100).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{30}H_{33}NOP_2$: 485.2037; found: 485.2034.

_P_-[2-(Diphenylphosphino)phenyl]-_N_,_N_-diisobutyl-_P_-phenylphosphinic Amide (2c)

Compound **2c** was synthesised from **1c** (300 mg, 0.91 mmol) and Ph_2PCl (196 μL, 1.09 mmol). Addition of the anion soln to a soln of the electrophile Ph_2PCl in THF (10 mL) was carried out to increase the yield of the product.

Yield: 47%; white foam; R_f = 0.40 (hexanes–EtOAc, 2:1).

IR ($CHCl_3$): 3017, 2402, 1202, 667 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91–7.82 (m, 1 H), 7.75–7.68 (m, 2 H), 7.46–7.11 (m, 16 H), 3.06–2.85 (m, 4 H), 1.99–1.85 (m, 4 H), 0.88 (d, *J* = 6.6 Hz, 6 H), 0.79 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.4 (dd, *J* = 26.2, 12.1 Hz, 1 C), 138.3 (dd, *J* = 122.9, 29.0 Hz, 1 C), 138.6 (d, *J* = 14.7 Hz, 1 C), 137.8 (d, *J* = 14.7 Hz, 1 C), 136.4 (d, *J* = 12.5 Hz, 1 C), 133.4 (d, *J* = 127.4 Hz, 1 C), 133.6 (d, *J* = 13.2 Hz, 2 C), 133.4 (d, *J* = 12.4 Hz, 2 C), 133.2–133.1 (m, 1 C), 132.6 (d, *J* = 9.2 Hz, 1 C), 131.5 (d, *J* = 9.4 Hz, 1 C), 130.9 (d, *J* = 2.6 Hz, 1 C), 130.8 (d, *J* = 2.5 Hz, 1 C), 128.0–127.6 (m, 9 C), 54.4 (s, *J* = 4.3 Hz, 2 C), 26.7 (d, *J* = 3.2 Hz, 2 C), 20.6 (s, 2 C), 20.4 (s, 2 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 34.3 (d, *J* = 2.7 Hz, 1 P), –9.5 (d, *J* = 3.0 Hz, 1 P).

MS (CI): *m*/*z* (%) = 514 (90) $[M + H]^+$, 385 (100).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{32}H_{37}NOP_2$: 513.2350; found: 513.2362.

_P_-[2-(Dicyclohexylphosphino)phenyl]-_N_,_N_-diethyl-_P_-phenylphosphinic Amide (2d)

Compound **2d** was synthesised from **1a** (516 mg, 1.89 mmol) and Cy_2PCl (2.27 mmol). Addition of the anion soln to a soln of the electrophile Cy_2PCl in THF (10 mL) was carried out to increase the yield of the product.

Yield: 45%; clear oil; R_f = 0.46 (hexanes–EtOAc, 2:1).

IR ($CHCl_3$): 3016, 2402, 1520, 722 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$); δ = 7.63–7.56 (m, 4 H), 7.43–7.30 (m, 5 H), 3.13–3.03 (m, 4 H), 1.90–1.07 (m, 22 H), 1.00 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.0 (dd, *J* = 31.3, 14.0 Hz, 1 C), 140.8 (dd, *J* = 124.9, 28.8 Hz, 1 C), 137.2 (dd, *J* = 121.8, 1.1 Hz, 1 C), 133.6 (br d, *J* = 12.4 Hz, 1 C), 132.6 (dd, *J* = 11.5, 8.1 Hz, 1 C), 131.5 (d, *J* = 9.8 Hz, 2 C), 130.0 (d, *J* = 2.6 Hz, 1 C), 126.9 (d, *J* = 2.6 Hz, 1 C), 127.3 (d, *J* = 12.7 Hz, 2 C), 126.9 (d, *J* = 12.1 Hz, 1 C), 46.8 (d, *J* = 4.6 Hz, 2 C), 35.2 (dd, *J* = 109.1, 18.4 Hz, 2 C), 30.3–23.3 (m, 10 C), 22.8 (d, *J* = 2.0 Hz, 2 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 34.6 (d, *J* = 8.9 Hz, 1 P), –7.8 (br s, 1 P).

MS (CI): *m*/*z* (%) = 470 (100) $[M + H]^+$, 397 (45), 386 (95).

HRMS (EI, 70 eV): *m*/*z* $[M – H]^+$ calcd for $C_{28}H_{40}NOP_2$: 469.2585; found: 469.2589.

_P_-[2-(Dicyclohexylphosphino)phenyl]-_N_,_N_-diisopropyl-_P_-phenylphosphinic Amide (2e)

Compound **2e** was synthesised from **1b** (569 mg, 1.89 mmol) and Cy_2PCl (2.27 mmol). Addition of the anion soln to a soln of the electrophile Cy_2PCl in THF (10 mL) was carried out to increase the yield of the product.

Yield: 51%; white foam; R_f = 0.66 (hexanes–EtOAc, 3:1).

IR ($CHCl_3$): 3015, 2402, 1524, 722 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.94–7.87 (m, 1 H), 7.69–7.61 (m, 1 H), 7.60 (dd, *J* = 11.7, 7.5 Hz, 2 H), 7.50–7.33 (m, 5 H), 3.49 (sept, *J* = 6.6 Hz, 1 H), 3.43 (sept, *J* = 6.6 Hz, 1 H), 2.03–1.22 (m, 22 H), 1.37 (d, *J* = 6.6 Hz, 6 H), 1.15 (d, *J* = 6.6 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.0 (dd, *J* = 31.3, 14.0 Hz, 1 C), 140.8 (dd, *J* = 124.9, 28.8 Hz, 1 C), 137.2 (dd, *J* = 121.8, 1.1 Hz, 1 C), 133.6 (d, *J* = 12.4 Hz, 1 C), 132.6 (dd, *J* = 11.5, 8.1 Hz, 1 C), 131.5 (d, *J* = 9.8 Hz, 2 C), 130.0 (d, *J* = 2.6 Hz, 1 C), 129.6 (d, *J* = 2.6 Hz, 1 C), 127.3 (d, *J* = 12.7 Hz, 2 C), 126.9 (d, *J* = 12.1 Hz, 1 C), 46.8 (d, *J* = 4.6 Hz, 2 C), 35.5 (dd, *J* = 109.1, 18.4 Hz, 1 C), 30.3–23.3 (m, 11 C), 23.0 (d, *J* = 2.0 Hz, 4 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.5 (d, *J* = 10.5 Hz, 1 P), –9.4 (br s, 1 P).

MS (CI): *m*/*z* (%) = 497 $[M + H]^+$, 414 (100).

HRMS (EI, 70 eV): *m*/*z* $[M – H]^+$ calcd for $C_{30}H_{44}NOP_2$: 496.2898; found: 496.2901.

_P_-[2-(Dicyclohexylphosphino)phenyl]-_N_,_N_-diisobutyl-_P_-phenylphosphinic Amide (2f)

Compound **2f** was synthesised from **1c** (612 mg, 1.89 mmol) and Cy_2PCl (2.27 mmol). Addition of the anion soln to a soln of the electrophile Cy_2PCl in THF (10 mL) was carried out to increase the yield of the product.

Yield: (43%); white foam; R_f = 0.45 (hexanes–EtOAc, 5:1).

IR ($CHCl_3$): 3015, 2402, 1524, 722 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (ddd, *J* = 11.7, 8.4, 1.5 Hz, 2 H), 7.68–7.54 (m, 2 H), 7.48–7.30 (m, 5 H), 3.05–2.82 (m, 6 H), 1.96–1.07 (m, 22 H), 0.87 (d, *J* = 6.6 Hz, 6 H), 0.77 (d, *J* = 6.6 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.6 (dd, *J* = 30.2, 12.1 Hz, 1 C), 139.9 (dd, *J* = 122.8, 29.1 Hz, 1 C), 135.1 (d, 1 C, *J* = 128.3), 133.6 (d, *J* = 13.1 Hz, 1 C), 133.2 (dd, *J* = 12.6, 8.6 Hz, 1 C), 132.9 (2 × d, *J* = 9.6, 9.1 Hz, 2 C), 130.7 (d, *J* = 2.5 Hz, 1 C), 130.0 (d, *J* = 2.6 Hz, 1 C), 127.7 (d, *J* = 12.6 Hz, 2 C), 127.2 (d, *J* = 12.6 Hz, 1 C), 54.7 (s, 2 C), 35.3 (dd, *J* = 16.7, 7.5 Hz, 2 C), 30.8–26.8 (m, 10 C), 26.3 (s, 2 C), 20.8 (s, 2 C), 20.4 (s, 2 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.9 (d, *J* = 10.7 Hz, 1 P), –9.6 (br s, 1 P).

MS (CI): *m*/*z* (%) = 526 (100) $[M + H]^+$, 442 (75), 397 (50).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{32}H_{48}NOP_2$: 525.3211; found: 525.3186.

P-{2-[Bis(2-methylphenyl)phosphino]phenyl}-*N*,*N*-diethyl-*P*-phenylphosphinic Amide (2g)

Compound **2g** was synthesised from **1a** (300 mg, 1.10 mmol) and $(2\text{-}MeC_6H_4)_2PCl$ (1.2 mmol). Addition of the anion soln to a soln of the electrophile $(2\text{-}MeC_6H_4)_2PCl$ in THF (10 mL) was needed to increase the yield of the product. Extraction and chromatography were performed as described in the above general procedure.

Yield: 48%; pale yellow foam; R_f = 0.52 (hexanes–EtOAc, 10:1).

IR ($CHCl_3$): 3022, 1203, 667 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.88 (m, 1 H), 7.61–7.55 (m, 1 H), 7.43–6.88 (m, 14 H), 6.60–6.57 (m, 1 H), 3.11–2.93 (m, 4 H), 2.26 (s, 3 H), 2.02 (s, 3 H), 1.01 (t, *J* = 7.2 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.8 (dd, *J* = 27.2, 17.5 Hz, 1 C), 142.0 (dd, *J* = 37.6, 12.8 Hz, 2 C), 138.3 (dd, *J* = 125.2, 29.3 Hz, 1 C), 136.2 (dd, *J* = 46.8, 14.4 Hz, 2 C), 136.2 (dd, *J* = 23.5, 12.2 Hz, 1 C), 133.5 (dd, *J* = 10.3, 7.4 Hz, 2 C), 133.5 (d, *J* = 7.4 Hz, 2 C), 133.3 (s, 1 C), 133.0 (d, *J* = 125.8 Hz, 1 C), 132.0 (dd, *J* = 9.4, 2.6 Hz, 2 C), 131.1 (d, *J* = 2.6 Hz, 1 C), 130.5 (d, *J* = 2.6 Hz, 1 C), 129.8 (dd, *J* = 8.7, 4.4 Hz, 2 C), 128.0 (d, *J* = 3.2 Hz, 2 C), 128.0 (d, *J* = 11.9 Hz, 1 C), 127.5 (d, *J* = 12.5 Hz, 2 C), 125.5 (d, *J* = 5.7 Hz, 2 C), 39.3 (d, *J* = 3.5 Hz, 2 C), 21.3 (d, *J* = 22.2 Hz, 1 C), 20.9 (d, *J* = 21.1 Hz, 1 C), 13.9 (d, *J* = 5.4 Hz, 2 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.2 (d, *J* = 5.0 Hz, 1 P), –24.9 (d, *J* = 5.0 Hz, 1 P).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{30}H_{33}NOP_2$: 485.2028; found: 485.2037.

P-{2-[Bis(2-methylphenyl)phosphino]phenyl}-*N*,*N*-diisopropyl-*P*-phenylphosphinic Amide (2h)

Compound **2h** was synthesised from **1b** (300 mg, 1.00 mmol) and $(2\text{-}MeC_6H_4)_2PCl$ (1.2 mmol). Addition of the anion soln to a soln of the electrophile $(2\text{-}MeC_6H_4)_2PCl$ in THF (10 mL) was needed to increase the yield of the product. Extraction and chromatography were performed as described in the above general procedure.

Yield: 48%; pale yellow foam; R_f = 0.45 (hexanes–EtOAc, 7:3).

IR ($CHCl_3$): 3026, 1212, 793 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96–7.89 (m, 1 H), 7.41–6.81 (m, 1 H), 6.60–6.57 (m, 14 H), 6.46–6.42 (m, 1 H), 3.41–3.31 (m, 2 H), 2.11 (s, 3 H), 1.77 (s, 3 H), 1.18 (d, *J* = 6.6 Hz, 6 H), 0.98 (d, *J* = 6.9 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4 (dd, *J* = 40.4, 27.0 Hz, 1 C), 141.4 (dd, *J* = 27.0, 23.9 Hz, 2 C), 140.5 (dd, *J* = 134.6, 27.1 Hz, 1 C), 137.1 (d, *J* = 10.6 Hz, 1 C), 136.4 (dd, *J* = 100.2, 12.3 Hz, 2 C), 135.5 (d, *J* = 119.8 Hz, 1 C), 133.4 (s, 1 C), 132.6 (s, 1 C), 132.9 (dd, *J* = 10.3, 7.8 Hz, 2 C), 131.6 (d, *J* = 9.7 Hz, 2 C), 131.0 (d, *J* = 2.9 Hz, 1 C), 130.2 (d, *J* = 2.6 Hz, 1 C), 129.8 (dd, *J* = 9.1, 4.3 Hz, 2 C), 128.0 (d, 2 C, 11.4 Hz), 127.8 (d, *J* = 10.8 Hz, 1 C), 127.3 (d, *J* = 12.2 Hz, 2 C), 125.4 (d, *J* = 2.0 Hz, 2 C), 47.0 (d, *J* = 4.6 Hz, 2 C), 23.2 (t, *J* = 5.0 Hz, 4 C), 21.5 (d, *J* = 23.1 Hz, 1 C), 20.9 (d, *J* = 20.9 Hz, 1 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.2 (d, *J* = 9.4 Hz, 1 P), –25.0 (br s, 1 P).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{32}H_{37}NOP_2$: 513.2359; found: 513.2350.

P-{2-[Bis(2-ethylphenyl)phosphino]phenyl}-*N*,*N*-diethyl-*P*-phenylphosphinic Amide (2i)

Compound **2i** was synthesised from **1a** (500 mg, 1.83 mmol) and $(2\text{-}EtC_6H_4)_2PCl$ (3.66 mmol, 2 equiv). Addition of the anion soln to a soln of the electrophile in THF (10 mL) was needed to increase the yield of the product. Extraction and chromatography were performed as described in the above general procedure.

Yield: 62%; white foam; R_f = 0.43 (hexanes–EtOAc, 1:1)

IR ($CHCl_3$): 3007, 1185, 754 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.86 (m, 1 H), 7.64–7.58 (m, 2 H), 7.36–7.02 (m, 10 H), 6.96–6.91 (m, 1 H), 6.85 (t, *J* = 7.2 Hz, 1 H), 6.69–6.62 (m, 2 H), 3.06–2.88 (m, 4 H), 2.73–2.55 (m, 2 H), 2.43–2.33 (m, 2 H), 1.05 (t, *J* = 7.5 Hz, 3 H), 1.01 (t, *J* = 7.1 Hz, 6 H), 0.85 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.8 (dd, *J* = 17.9, 17.4 Hz, 2 C), 142.8 (dd, *J* = 12.8, 12.8 Hz, 1 C), 138.2 (dd, *J* = 30.0, 29.5 Hz, 1 C), 136.5 (d, *J* = 12.5 Hz, 2 C), 136.2 (d, *J* = 15.1 Hz, 1 C), 135.7 (d, *J* = 14.5 Hz, 2 C), 133.5 (d, *J* = 17.3 Hz, 2 C), 133.2 (d, *J* = 17.1 Hz, 2 C), 132.9 (d, *J* = 124.4 Hz, 1 C), 131.9 (dd, *J* = 8.9, 9.5 Hz, 2 C), 130.6 (dd, *J* = 22.5, 19.7 Hz, 1 C), 128.1 (d, *J* = 3.0 Hz, 2 C), 127.6 (d, *J* = 5.3 Hz, 2 C), 127.3 (d, *J* = 12.8 Hz, 2 C), 125.2 (d, *J* = 10.5 Hz, 2 C), 39.1 (d, *J* = 3.5 Hz, 2 C), 26.9 (2xd, *J* = 14.9, 15.9 Hz, 2 C), 14.6 (d, *J* = 3.9 Hz, 2 C), 13.7 (d, *J* = 3.38 Hz, 2 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 33.6 (d, *J* = 4.5 Hz, 1 P), –27.3 (d, *J* = 4.6 Hz, 1 P).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{32}H_{37}NOP_2$: 513.5972; found: 513.5803.

P-{2-[Bis(2,3-dimethylphenyl)phosphino]phenyl}-*N*,*N*-diethyl-*P*-phenylphosphinic Amide (2j)

Compound **2j** was synthesised from **1a** (300 mg, 1.10 mmol) and *o*-xylyl$_2$PCl (3.66 mmol). Addition of the anion soln to a soln of the electrophile in THF (10 mL) was needed to increase the yield of the product. Extraction and chromatography were performed as described in the above general procedure.

Yield: 58%; pale yellow foam; R_f = 0.48 (hexanes–EtOAc, 7:3).

IR ($CHCl_3$): 3030, 1206, 710 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95–7.87 (m, 1 H), 7.60–7.53 (m, 2 H), 7.44–7.00 (m, 9 H), 6.90–6.79 (m, 2 H), 6.45–6.12 (m, 2 H), 3.13–2.95 (m, 4 H), 2.19 (d, *J* = 12.3 Hz, 12 H), 1.02 (t, *J* = 3.4 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.5 (dd, *J* = 24.2, 18.6 Hz, 2 C), 136.8 (dd, *J* = 37.6, 12.8 Hz, 2 C), 133.4 (d, *J* = 46.4, 27.3 Hz, 2 C), 132.2 (d, *J* = 49.7 Hz, 1 C), 131.5 (dd, *J* = 32.2, 12.2 Hz, 2 C), 131.3 (d, *J* = 21.5, 7.4 Hz, 2 C), 131.1 (d, *J* = 7.3 Hz, 2 C), 130.6 (d, *J* = 30.2 Hz, 1 C), 129.9 (d, *J* = 125.8 Hz, 1 C), 129.3 (d, *J* = 2.6 Hz, 2 C), 128.0 (d, *J* = 2.6 Hz, 2 C), 127.6 (d, *J* = 2.6 Hz, 2 C) ,127.5 (d, *J* = 2.6 Hz, 2 C), 125.7 (d, *J* = 4.2 Hz, 2 C), 125.3 (d, *J* = 4.6 Hz, 1 C), 125.2 (d, *J* = 12.5 Hz, 2 C), 121.9 (d, *J* = 5.7 Hz, 1 C), 39.4 (d, *J* = 7.5 Hz, 2 C), 20.6 (d, *J* = 22.4 Hz, 1 C), 17.9 (d, 1 C, *J* = 25.0), 17.1 (d, *J* = 27.6 Hz, 1 C), 17.0 (d, 1 C, *J* = 26.7), 13.9 (d, *J* = 3.15 Hz, 2 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 34.1 (d, *J* = 6.1 Hz, 1 P), –23.5 (d, *J* = 5.3 Hz, 1 P).

HRMS (EI, 70 eV): *m/z* calcd for $C_{32}H_{37}NOP_2$: 513.5908; found: 513.5705.

_P_-[4-(Dimethylamino)-2-(diphenylphosphino)phenyl]-_P_-[4-(dimethylamino)phenyl]-_N_,_N_-diisopropylphosphinic Amide (2k)

Compound **2k** was synthesised from *N*,*N*-diisopropyl-*P*,*P*-bis[4-(dimethylamino)phenyl]phosphinic amide (300 mg, 0.78 mmol) and Ph_2PCl (168 μL, 0.94 mmol). Addition of the anion soln to a soln of the electrophile in THF (10 mL) was carried out to increase the yield of the product.

Yield: 73%; white foam; R_f = 0.40 (hexanes–EtOAc, 2:1).

IR ($CHCl_3$): 3015, 2400, 667 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.92 (m, 1 H), 7.60–7.52 (m, 2 H), 7.39–7.01 (m, 13 H), 6.62 (d, *J* = 7.2 Hz, 2 H), 3.41 (sept, *J* = 6.9 Hz, 2 H), 2.90 (s, 12 H), 1.30 (d, *J* = 6.9 Hz, 6 H), 1.14 (d, *J* = 6.6 Hz, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.3 (d, *J* = 2.3 Hz, 1 C), 150.8 (d, *J* = 2.3 Hz, 1 C), 143.4 (dd, *J* = 26.2, 14.1 Hz, 1 C), 139.7 (d, *J* = 15.2 Hz, 1 C), 139.0 (d, *J* = 15.2 Hz, 1 C), 134.7 (dd, *J* = 11.7, 7.4 Hz, 1 C), 133.9 (d, *J* = 5.2 Hz, 2 C), 133.6 (d, *J* = 4.6 Hz, 4 C), 129.7 (dd, *J* = 133.0, 11.5 Hz, 1 C), 127.7–127.4 (m, 6 C), 121.7 (d, *J* = 133.5 Hz, 1 C), 119.7 (d, *J* = 13.3 Hz, 1 C), 110.6 (d, *J* = 13.3 Hz, 2 C), 110.1 (d, *J* = 12.6 Hz, 1 C), 47.0 (d, *J* = 4.3 Hz, 2 C), 39.9 (s, 2 C), 39.5 (s, 2 C), 23.5 (d, *J* = 2.6 Hz, 2 C), 23.4 (d, *J* = 2.3 Hz, 2 C).

^{31}P NMR (121 MHz, $CDCl_3$): δ = 34.8 (d, *J* = 1.9 Hz, 1 P), –7.4 (d, *J* = 2.2 Hz, 1 P).

MS (CI): *m/z* (%) = 572 (60) $[M + H]^+$, 471 (100).

HRMS (EI, 70 eV): *m/z* calcd for $C_{34}H_{43}N_3OP_2$: 571.2881; found: 571.2861.

Suzuki Reactions; General Procedure

The phosphine ligand (1 or 2 equiv with respect to Pd, as required) and $Pd(OAc)_2$ (1 mg, 4.45 μmol) were dissolved in toluene (10 mL). The soln was allowed to stir for 20 min at r.t. K_3PO_4 (2 equiv, 8.9 mmol), the aryl halide ArX (1 equiv, 4.45 mol), and $PhB(OH)_2$ (1.5 equiv, 6.67 mmol) were then added, and the reaction mixture was stirred at the required temperature for 24 h. EtOAc (10 mL) was then added and the reaction mixture was filtered through a small amount of silica and the products were analysed by GC-FID (toluene internal standard). All of the Suzuki products have been prepared and fully characterised previously (or are commercially available).

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