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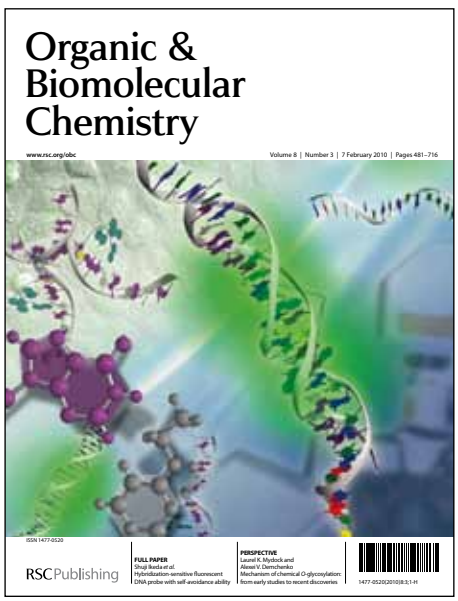

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Synthesis and characterisation of novel *o*-xylene-based *P,E* ligands †

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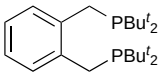
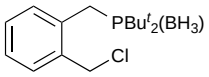
A range of novel hybrid ligands of the type, *o*-$C_6H_4(CH_2PBu^t{}_2)(CH_2E)$ (E = $P(C_6F_5)_2$, SBu^t, SPh, $S(O)Bu^t$, NMe_2, $SiPh_2H$), have been synthesised in two or three steps from the common substrate, *o*-$C_6H_4\{CH_2PBu^t{}_2(BH_3)\}(CH_2Cl)$. The initial step involved treatment of the substrate with the appropriate nucleophilic reagent, or preparation of a Grignard reagent from *o*-$C_6H_4\{CH_2PBu^t{}_2(BH_3)\}(CH_2Cl)$ and reaction with the appropriate electrophile. In most cases, this versatile strategy produced air-stable crystalline ligand precursors. Phosphine deprotection was achieved *via* one of three methods, dependent upon the properties of the second functional group. An alternative synthesis of the known ligand, *o*-$C_6H_4(CH_2PBu^t{}_2)(CH_2PPh_2)$, is also presented.

Introduction

Phosphine ligands are ubiquitous in the field of homogeneous catalysis, and there are many examples of phosphine ligands as integral components of industrial catalysts. One example of this is the chelating diphosphine ligand *o*-$C_6H_4(CH_2PBu^t{}_2)_2$ (**dbpx**), which was instrumental in the development of a palladium catalyst for the methoxycarbonylation of ethene on a multi-tonne scale.[1–3] As a result of this commerical success, a lot of interest has been generated in diphosphine ligands containing *o*-xylene backbones. A number of patents have subsequently been granted for catalytic processes that utilise dbpx,[4–8] and the use of phosphine substituents other than *t*-butyl groups has also been investigated.[9–12] There are also recent examples of unsymmetrical diphosphine ligands of this type, where the substituents on each phosphorus atom are different.[13–18]



dbpx



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Another area of active investigation is that of hybrid *P,E* ligands,[19,20] due to the ability of these ligands to produce different chemical environments *trans* to the donor atoms in metal complexes, and their potential for hemilability. However, to the best of our knowledge, there are currently no known examples of heterobidentate *P,E* ligands containing *o*-xylene backbones.

We recently reported the synthesis of a potentially versatile new substrate for the production of unsymmetrical diphosphine ligands, *o*-$C_6H_4\{CH_2PBu^t{}_2(BH_3)\}(CH_2Cl)$ (**1**).[21] In this paper we use compound **1** to present an alternative methodology for the production of unsymmetrical diphosphine ligands, and also for the synthesis of a number of novel compounds for use as phosphine-thioether, phosphine-sulfoxide, phosphine-amine and phosphine-silane hybrid ligands.

Unlike the currently used methodology,[13] which depends upon two sequential nucleophilic substitution steps, compound **1** does not require the availability of a second nucleophile to produce unsymmetrical ligands. The reactivity of the benzyl chloride moiety in **1** can be reversed by conversion to a Grignard reagent, which can then be reacted with electrophilic reagents to synthesise compounds that would otherwise be inaccessible. In most cases, the route from compound **1** also has the benefit of providing air-stable, crystalline ligand precursors, which can be easily stored for many months without decomposition.

Results and Discussion

P,P Compounds

The known ligand *o*-$C_6H_4(CH_2PBu^t{}_2)(CH_2PPh_2)$ (**3**) has been synthesised from **1** in two steps (Scheme 1). Compound **1** was treated with lithium diphenylphosphide–borane and the product (**2**) crystallised in 57% yield. Borane protection of

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both phosphines renders this material completely air-stable and allows compound **2** to be stored under ambient conditions for long periods of time. The $^{31}P\{^{1}H\}$ NMR spectrum of this compound displays broad peaks (due to boron coupling) centred at 47.7 and 18.5 ppm, indicative of benzyldi-*t*-butylphosphine–borane and benzyldiphenylphosphine–borane moieties respectively.[22]

Compound **2** was easily deprotected by heating to 100 °C for one hour in excess morpholine, to give ligand **3** after work up in good yield and high purity. Complete disappearance of the broad peaks in the $^{31}P\{^{1}H\}$ NMR spectrum, and appearance of sharp doublets ($^{5}J_{PP}$ = 1.4 Hz) at 24.5 and −15.6 ppm, for the deprotected PBu^{t}_{2} and PPh_2 groups respectively, is in agreement with the published NMR data for compound **3**.[15]

In some instances, the above synthetic route is not viable as the appropriate nucleophilic reagent to produce the desired compound is unavailable. For example, the bis(pentafluorophenyl)phosphide anion is unstable even at low temperatures.[23] In order to synthesise a molecule containing a bis(pentafluorophenyl)phosphine group (*i.e.* compound **4**), the *ortho*-substituted benzyl chloride compound **1** was treated with magnesium powder in THF to generate an *ortho*-substituted benzyl Grignard reagent. This solution was then combined with $(C_6F_5)_2PBr$ to produce the borane-protected unsymmetric diphosphine compound **4** (Scheme 2). The $^{31}P\{^{1}H\}$ NMR spectrum of this compound displays the characteristic broad di-*t*-butylphosphine–borane peak at 49.4 ppm, and a bis(pentafluorophenyl)phosphine quintet at −50.5 ppm. Deprotection of compound **4** was achieved by treatment with tetrafluoroboric acid (Scheme 3), giving novel ligand **5** in moderate yield. Again, the presence of a sharp doublet and quintet of doublets (at 25.2 and −50.9 ppm respectively) in the $^{31}P\{^{1}H\}$ NMR spectrum of compound **5** confirmed complete removal of the borane protecting group.

Deprotection of compound **4** was also attempted with excess morpholine. Interestingly, along with the desired deprotection, nucleophilic aromatic substitution occurred at the *para* position of each pentafluorophenylphosphine, producing a clean sample of novel compound **6** (Scheme 3). This type of nucleophilic aromatic substitution has previously been shown to occur between pentafluorophenyl substituents of various compounds and morpholine;[24–26] however, this is the first example of nucleophilic aromatic substitution at the *para* position of a pentafluorophenylphosphine by a secondary amine.

P,S Compounds

For a long time, sulfur compounds were not considered viable ligands for use in homogeneous catalysis, as they were widely believed to poison catalysts.[27,28] More recently they have become the focus of research in catalysis[29] and other areas,[30] nevertheless they remain relatively unexplored compared with other donor atom types.[31]

The synthesis of phosphine-thioether compounds with an *o*-xylene backbone is quite straightforward. Compound **1** was treated with an excess of the appropriate sodium thiolate precursor to produce compounds containing either an electron-rich (**7a**) or electron-poor (**7b**) thioether moiety in good yield (Scheme 4). $^{11}B\{^{1}H\}$ NMR spectra of these compounds was collected, displaying peaks with doublet coupling ($^{1}J_{PB} \approx 48$ Hz) centred at −40.4 and −40.7 ppm for compounds **7a** and **7b** respectively.

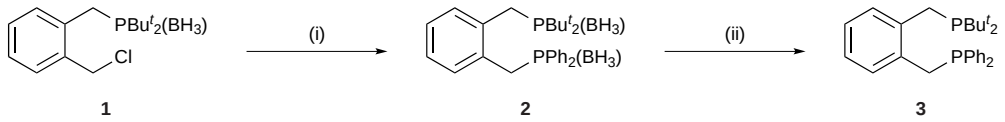
Synthesis of the equivalent phosphine-sulfoxide compounds is more difficult, as standard peroxide-based oxidising agents are known to deprotect and oxidise trialkylphosphine–boranes,[32,33] and nucleophilic sulfoxide reagents are not available. However, a PCC derivative, 3-carboxypyridinium chlorochromate (CPCC), is known to selectively oxidise thioethers to sulfoxides in the presence of functional groups.[34] In this case, CPCC oxidised compound **7a** to the racemic borane-protected phosphine-sulfoxide **8** in a 58% yield (Scheme 5). As the sulfur atom in compound **8** is a chiral centre, the methylene protons and phosphine *t*-butyl groups are rendered diastereotopic, which is reflected in the doubling of ^{1}H and ^{13}C NMR signals for these atoms when compared with the precursor.

Again, these phosphine-borane compounds were easily deprotected by heating to 100 °C for one hour in excess morpholine, producing novel ligands **9a**, **9b** and **10** with high purity and moderate to good yield (Scheme 6). The complete deprotection of these compounds was again established by the appearance of sharp singlet peaks in the $^{31}P\{^{1}H\}$ NMR spectra between 25.0 and 25.9 ppm.

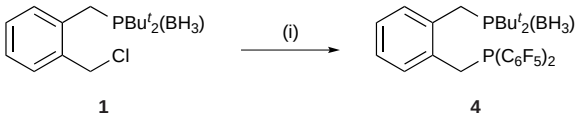
P,N Compounds

Both phosphorus and nitrogen donor atoms are widely used in coordination chemistry. The combination of the two to form hybrid *P,N* ligands has recently attracted a great deal of interest in the field, due to their interesting coordination behaviour[35,36] and catalytic applications.[35,37]

As the addition of a lithium amide reagent to compound **1** would result in deprotection of the phosphine–borane, it is necessary to borane-protect the amine prior to reaction with



Scheme 1 *Reagents and conditions:* (i) LiPPh$_2$(BH$_3$), THF, −78 °C → rt, overnight, 57% yield; (ii) Morpholine, 100 °C, 1 h, 82% yield.



Scheme 2 *Reagents and conditions:* (i) Mg powder, (C$_6$F$_5$)$_2$PBr, THF, 0 °C → rt, overnight, 32% yield.

compound **1**. Lithium *N,N*-dialkylaminoborohydride (LAB) reagents are well-known reducing agents when utilised at room temperature or above; however, at or below 0 °C, LAB reagents can react with benzyl halides to produce tertiary amine–boranes.[38] Using this methodology, compounds **11a–c** were synthesised in yields of over 80%, even when the LAB reagent contained bulkier ethyl substituents (Scheme 7). The ^{1}H NMR spectra of these compounds display very broad peaks centred around 2.2 and 1.2 ppm, for the amine–borane and phosphine–borane protons respectively. The ^{11}B{^{1}H} NMR spectra of these compounds also display two peaks, a singlet for the amine–borane and the expected doublet for the phosphine–borane.

These phosphine-amine compounds also require a different deprotection strategy, as morpholine does not efficiently deprotect the amine–borane moiety. An effective deprotection strategy for compounds **11a–c** involves treatment with tetrafluoroboric acid, followed by sodium hydrogen carbonate, to give novel ligands **12a–c** in moderate to good yield with high purity (Scheme 7). Deprotection of both the phosphorus and nitrogen atoms was established by the complete absence of any broad peaks associated with BH$_3$ protons in the ^{1}H NMR spectra of the ligands.

P,Si Compounds

Over recent decades, silyl ligands have attracted interest as they are considered to have a great impact on the various parameters of transition metal complexes, which may lead to interesting and beneficial reactivity patterns.[39] However, metal-silicon bonds are highly reactive. One method of reducing this unwanted reactivity is to employ the chelate effect, for example through the use of *P,Si* chelating ligands.

In general, secondary silyl anions are unstable. The only known examples are LiSiMes$_2$H and LiSiPh$_2$H (produced in low yield).[40] For this reason, a better route to phosphine-silane compounds such as **14**, is *via* an *in situ* benzyl Grignard reagent. Compound **1** was combined with excess magnesium turnings and chlorodiphenylsilane in THF under anhydrous conditions and stirred at room temperature overnight, to give the borane-protected phosphine-silane compound **13**, as shown in Scheme 8. The ^{31}P{^{1}H} NMR spectrum of compound **13** displayed the expected broad peak centred at 48.6 ppm, and the existence of a triplet peak at 5.10 ppm with silicon satellites ($^1J_{SiH}$ = 197.3 Hz) in the ^{1}H NMR spectrum confirmed the presence of the Si−H bond.

Removal of the borane protecting group from compound **13** was attempted with morpholine but resulted in a mixture of products, and as Si−H bonds are known to undergo acid hydrolysis,[41] an alternative deprotection method was required. To this end, compound **13** and DABCO were dissolved in toluene and heated to 60 °C overnight (Scheme 8). This procedure gave ligand **14** in 69% yield with high purity. Again, the presence of a triplet peak at 5.22 ppm in the ^{1}H NMR spectrum, also with silicon sateliites, confirmed the Si−H bond remained intact.

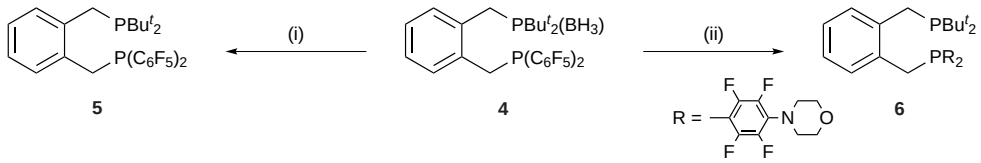
The overall yields of all *P,E* ligands synthesised in two or three steps from compound **1** are shown in Table 1.

Table 1 Overall yields of *P,E* ligands from compound **1**.

Ligand	E	Yield (%)
3	PPh$_2$	47
5	P(C$_6$F$_5$)$_2$	16
6	P{(C$_6$F$_4$)N(CH$_2$CH$_2$)$_2$O}$_2$	27
9a	SBu^t	74
9b	SPh	52
10	S(O)Bu^t	38
12a	NMe$_2$	68
12b	N(CH$_2$)$_4$	53
12c	NEt$_2$	58
14	SiPh$_2$H	23

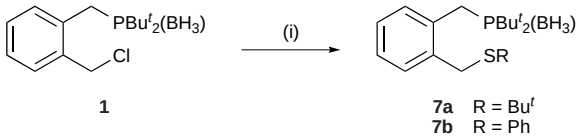
NMR Comparison

Common ^{1}H and ^{31}P NMR data for the novel *o*-C$_6$H$_4${CH$_2$PBu$^t_2$(BH$_3$)}(CH$_2$E) compounds is shown in Table 2. The signals corresponding to the PBu$^t_2$(BH$_3$) moieties show little variation, for example the broad ^{31}P NMR



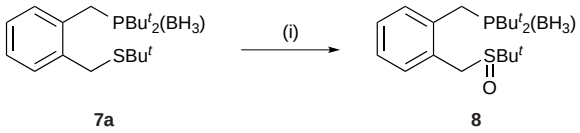
5 4 6

Scheme 3 *Reagents and conditions:* (i) $HBF_4 \cdot Et_2O$, CH_2Cl_2, rt, 1 h, $NaHCO_3$, H_2O, rt, 30 min, 51% yield; (ii) Morpholine, 100 °C, 1 h, 86% yield.



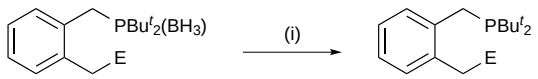
1 **7a** R = Bu^t **7b** R = Ph

Scheme 4 *Reagents and conditions:* (i) NaSR, EtOH, rt, overnight, 75–80% yield.



7a **8**

Scheme 5 *Reagents and conditions:* (i) CPCC, $AlCl_3$, MeCN, reflux, 2 h, 58% yield.



7a E = SBu^t **9a** E = SBu^t
7b E = SPh **9b** E = SPh
8 E = S(O)Bu^t **10** E = S(O)Bu^t

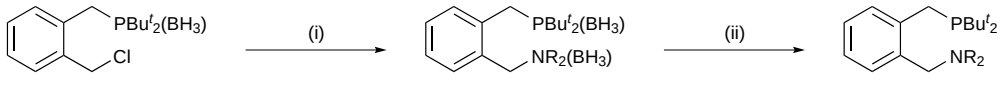
Scheme 6 *Reagents and conditions:* (i) Morpholine, 100 °C, 1 h, 69–92% yield.

signals range from 47.7 ppm (E = $PPh_2(BH_3)$) to 49.8 ppm (E = $NMe_2(BH_3)$, $NEt_2(BH_3)$), and the *t*-butyl ^{1}H NMR signals vary by only 0.20 ppm over the nine compounds. The shifts associated with the CH_2P groups are somewhat more influenced by the identity of substituent E, from δ_H 2.69 in compound **13** (E = $SiPh_2H$) to δ_H 4.07 in compound **8** (E = S(O)Bu^t). The AB system associated with the CH_2P protons of compound **8** is also the outlier in terms of the $^2J_{PH}$ coupling constants, with values of 9.0 and 15.0 Hz, as compared to $J \approx 12.0$ Hz for all the other borane-protected *P,E* compounds. As would be expected, the ^{1}H NMR chemical shifts of the signals associated with the CH_2E protons are also dependent upon the identity of E, varying from 2.93 ppm in compound **13** to 4.61 ppm in compound **8**. The $^{31}P\{^1H\}$ NMR signals associated with these phosphine–borane compounds do not show the expected 1:1:1:1 quartet due to ^{11}B coupling, but rather broad multiplet coupling. The peak shape changes with temperature, suggesting a dynamic process may exist, but this phenomenon has not been further investigated.

A number of dissimilarities in the ^{1}H and ^{31}P NMR data are observed upon removal of the borane protecting groups to give the *o*-$C_6H_4(CH_2PBu^t_2)(CH_2E)$ (*P,E*) ligands (Table 3). The greatest difference is seen in the ^{31}P NMR spectra, where the broad signals of the formerly $PBu^t_2(BH_3)$ moieties (*ca.* 49 ppm) are replaced by sharp singlets at *ca.* 25 ppm, corresponding to the free di-*t*-butylphosphine groups. Deprotection of the phosphine also has a significant effect on the $^2J_{PH}$ coupling constant of the signal associated with the CH_2P protons. These coupling constants are reduced from *ca.* 12 Hz in the phosphine-borane compounds, to < 3 Hz in the free phosphines. In fact, in many cases no $^2J_{PH}$ coupling is observed. However, in a number of the deprotected *P,E* ligands a long-range $^5J_{PH}$ coupling of up to 3.5 Hz is seen between the CH_2E protons and the di-*t*-butylphosphine. This feature is not present in the ^{1}H NMR spectra of any of the borane-protected compounds.

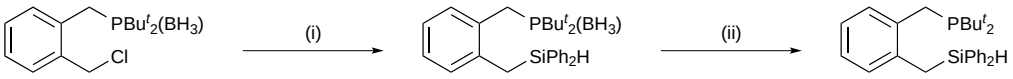
Conclusions

In summary, a number of novel diphosphine, phosphine-thioether, phosphine-sulfoxide, phosphine-amine and



1 **11a** R = Me; **11b** $R_2 = (CH_2)_4$; **11c** R = Et **12a** R = Me; **12b** $R_2 = (CH_2)_4$; **12c** R = Et

Scheme 7 *Reagents and conditions:* (i) $LiNR_2(BH_3)$, THF, −5 °C, 1 h, 80–89% yield; (ii) $HBF_4 \cdot Et_2O$, CH_2Cl_2, rt, 1 h, $NaHCO_3$, H_2O, rt, 30 min, 60–85% yield.



1 **13** **14**

Scheme 8 *Reagents and conditions:* (i) Mg turnings, I_2, Ph_2SiHCl, THF, rt, overnight, 34% yield; (ii) DABCO, toluene, 60 °C, overnight, 69% yield.

Table 2 Selected ^{31}P and ^{1}H NMR shifts (in ppm) and couplings (in Hz) of borane-protected *P,E* compounds in benzene-d_6.

		PBu^t			CH_2P		CH_2E
Compound	**E**	δ_P[a]	δ_H	$^3J_{PH}$	δ_H	$^2J_{PH}$	δ_H
2[b]	$PPh_2(BH_3)$	47.7	1.23	12.3	3.11	11.8	3.93
4	$P(C_6F_5)_2$	49.4	1.09	12.2	3.29	11.9	4.23
7a	SBu^t	47.9	1.12	12.5	3.27	12.0	3.99
7b	SPh	48.0	1.05	12.0	3.20	12.0	4.40
8	S(O)Bu^t	48.0	1.06 & 1.19	12.5 & 12.5	3.04 & 4.07	15.0 & 9.0	3.63 & 4.61
11a	$NMe_2(BH_3)$	49.8	1.08	12.0	3.55	12.0	3.98
11b	$N(CH_2)_4(BH_3)$	49.6	1.13	12.5	3.69	12.0	4.10
11c	$NEt_2(BH_3)$	49.8	1.12	12.5	3.82	12.0	4.02
13	$SiPh_2H$	48.6	1.03	12.2	2.69	12.0	2.93

[a]Broad multiplet coupling.
[b]Spectra recorded in chloroform-*d*.

Table 3 Selected ^{31}P and ^{1}H NMR shifts (in ppm) and couplings (in Hz) of *P,E* ligands in benzene-d_6.

		PBu^t			CH_2P		CH_2E	
Ligand	**E**	δ_P	δ_H	$^3J_{PH}$	δ_H	$^2J_{PH}$	δ_H	$^5J_{PH}$
3	PPh_2	24.5	1.09	10.5	3.09	–	3.92	–
5	$P(C_6F_5)_2$	25.2	1.07	10.8	3.07	–	4.27	–
6	$P\{(C_6F_4)N(CH_2CH_2)_2O\}_2$	25.4	1.12	10.7	3.20	–	4.53	–
9a	SBu^t	25.0	1.13	10.6	3.09	1.2	4.05	–
9b	SPh	25.9	1.07	10.8	3.06	–	4.51	2.2
10	S(O)Bu^t	25.2	1.06 & 1.14	10.9 & 10.8	2.99 & 3.37	2.0 & –	3.85 & 4.25	1.4 & 3.5
12a	NMe_2	24.5	1.13	10.7	3.16	2.4	3.60	–
12b	$N(CH_2)_4$	24.6	1.14	10.5	3.16	2.7	3.82	–
12c	NEt_2	23.8	1.14	10.8	3.12	2.7	3.69	–
14	$SiPh_2H$	25.2	1.05	10.5	2.65	1.5	3.10	1.5

phosphine-silane hybrid ligands containing an *o*-xylene backbone were synthesised in two or three steps from the common substrate **1**. This versatile substrate was treated with a nucleophilic reagent or, where the appropriate nucleophile was unavailable, converted to a Grignard reagent and reacted with an electrophile. In most cases, the borane-protected ligand precursors formed from this procedure were crystalline and air-stable. Deprotection of the phosphine moiety was achieved by treatment with morpholine, tetrafluoroboric acid or DABCO, dependent upon the properties of the second functional group, producing a range of novel *P,E* ligands in moderate to good yield.

Experimental

General methods All reactions were carried out using degassed solvents and standard Schlenk techniques under a nitrogen or argon atmosphere unless stated otherwise. Starting materials were obtained from Sigma-Aldrich or Merck Chemical Companies. DABCO was sublimed under reduced pressure, and other amines and thiols were dried and distilled before use. Diphenylphosphine–borane,[42] α-(di-*t*-butylphosphino)-α'-chloro-*o*-xylene–borane (**1**),[21] bis(pentafluorophenyl)bromophosphine,[43] 3-carboxypyridinium chlorochromate,[34] pyrrolidine–borane[44] and diethylamine–borane[45] were synthesised using literature methods. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled under a nitrogen or argon atmosphere from sodium benzophenone ketyl immediately prior to use. All other solvents used were of analytical grade, and were degassed and dried over molecular sieves. Elemental analysis was performed at the Campbell Microanalytical Laboratory at Otago University, Dunedin. Infrared spectra were obtained using a Perkin-Elmer Spectrum One FT-IR spectrophotometer (resolution 4 cm^{-1}) in absorbance mode, as films from CH_2Cl_2. All spectral data were obtained at ambient temperature. Nuclear magnetic resonance (NMR) spectra were recorded using a Varian Unity Inova spectrometer operating at 300, 121 and 282 MHz for ^1H, ^{31}P and ^{19}F spectra respectively, a Varian Unity Inova spectrometer operating at 500, 125 and 96 MHz for ^1H, ^{13}C and ^{11}B spectra respectively, and a Varian DirectDrive spectrometer operating at 600 and 150 MHz for ^1H and ^{13}C spectra respectively. All direct-detected ^1H and ^{13}C chemical shifts, δ (ppm), were referenced to the residual solvent peak of the deuterated solvent.[46] ^{31}P, ^{19}F and ^{11}B NMR spectra were referenced to H_3PO_4, $CFCl_3$ and $BF_3 \cdot Et_2O$ respectively. ^{13}C, ^{31}P, ^{19}F and ^{11}B NMR spectra were measured with ^1H-decoupling. *J* values are given in Hz. Electrospray ionisation mass spectrometry was recorded using an Agilent 6530 Q-TOF mass spectrometer or performed by the Carbohydrate Chemistry Group at Industrial Research Limited, Lower Hutt, using a Waters Q-TOF Premier Tandem mass spectrometer.

α-(Di-*t*-butylphosphino)-α'-(diphenylphosphino)-*o*-xylene–diborane (2) A solution of freshly prepared diphenylphosphine–borane (0.136 g, 0.68 mmol) in THF (5 mL) was cooled to 0 °C and a solution of *n*-butyllithium (0.35 mL, 2.0 M in cyclohexane, 0.70 mmol) was added dropwise with stirring. The mixture was stirred at room temperature for 2 h, cooled to −78 °C and a solution of compound **1** (0.180 g, 0.60 mmol) in THF (4 mL) added. The mixture was stirred at room temperature overnight, the solvent removed under reduced pressure, and the resulting off-white solid stirred in toluene (25 mL) for 1 h in the air. Filtration and solvent removal under reduced pressure gave crude compound **2**, which was recrystallised from 1:3 toluene/*n*-hexane. Air-stable white crystals (0.158 g, 57%). Anal. found: C, 73.0; H, 9.0; calc. for $C_{28}H_{42}B_2P_2$: C, 72.8; H, 9.2%. IR ν_{max}/cm^{-1}: 2349–2386 (BH), 2869–3079 (CH). NMR δ_H (600 MHz; $CDCl_3$): 0.2–1.2 (6H, br, BH_3), 1.23 (18H, d, *J* 12.3, PBu^t), 3.11 (2H, d, *J* 11.8, CH_2PBu^t), 3.93 (2H, d, *J* 11.8, CH_2PPh), 6.51 (1H, d, *J* 7.6, Ar), 6.90 (1H, t, *J* 7.4, Ar), 7.10 (1H, t, *J* 7.6, Ar), 7.42 (5H, m, Ar & PPh), 7.50 (2H, m, PPh), 7.59 (4H, m, Ar); δ_C (150 MHz; $CDCl_3$): 23.54 (d, *J* 23.5, CH_2PBu^t), 28.55 (s, $PCMe_3$), 31.88 (d, *J* 31.1, CH_2PPh), 33.15 (d, *J* 24.8, $PCMe_3$), 126.50 (t, *J* 2.6, Ar), 126.88 (dd, *J* 3.2, 1.9, Ar), 128.81 (d, *J* 10.2, PPh), 129.10 (d, *J* 54.0, PPh), 131.41 (d, *J* 1.9, PPh), 131.60 (dd, *J* 3.8, 1.9, Ar), 131.78 (t, *J* 3.8, Ar), 132.03 (t, *J* 3.2, Ar), 132.80 (d, *J* 8.9, PPh), 134.66 (t, *J* 4.5, Ar); δ_P (121 MHz; $CDCl_3$): 18.52 (br, PPh), 47.69 (br, PBu^t). HRMS found: *m/z* 485.2848; calc. for $C_{28}H_{42}B_2NaP_2$ $[M+Na]^+$: 485.2850.

α-(Di-*t*-butylphosphino)-α'-{bis(pentafluorophenyl)phosphino}-*o*-xylene–borane (4) Flame-dried magnesium powder (1.20 g, 49 mmol) and THF (5 mL) were combined in a Schlenk tube, 1,2-dibromoethane (0.05 mL) added and the mixture heated until bubbles appeared. After reaction was complete, the solvent was decanted and fresh THF (5 mL) added. A solution of compound **1** (0.40 g, 1.34 mmol) in THF (5 mL) was added and the mixture stirred for 2 h. The resulting green solution was decanted and added dropwise to a solution of bis(pentafluorophenyl)bromophosphine (0.30 mL, 1.34 mmol) in THF (5 mL) at 0 °C. The solution was stirred at room temperature overnight and the solvent removed under reduced pressure giving a sticky solid. The mixture was triturated with *n*-hexane (40 mL), filtered through a plug of alumina and the solvent removed under reduced pressure. The resulting cloudy oil was washed with methanol (2 × 5 mL) giving compound **4**. Air-sensitive white powder (0.27 g, 32%). NMR δ_H (500 MHz; C_6D_6): 0.9–1.6 (6H, br, BH_3), 1.09 (18H, d, *J* 12.2, PBu^t), 3.29 (2H, d, *J* 11.9, CH_2PBu^t),

4.23 (2H, d, *J* 4.6, C*H*$_2$P(C$_6$F$_5$), 6.64 (1H, d, *J* 7.6, Ar), 6.69 (1H, t, *J* 7.6, Ar), 6.86 (1H, t, *J* 7.6, Ar), 7.51 (1H, d, *J* 7.8, Ar); δ_C (125 MHz; C$_6$D$_6$): 23.22 (dd, *J* 22.1, 9.1, *C*H$_2$PBu^t), 28.29 (s, PC*Me*$_3$), 30.20 (m, *C*H$_2$P(C$_6$F$_5$)), 33.08 (d, *J* 24.0, P*C*Me$_3$), 108.60 (m, P(C$_6$F$_5$)), 127.34 (t, *J* 2.4, Ar), 127.45 (dd, *J* 3.4, 1.5, Ar), 130.91 (d, *J* 8.6, Ar), 132.74 (t, *J* 2.9, Ar), 134.02 (dd, *J* 5.8, 4.3, Ar), 134.44 (t, *J* 3.8, Ar), 137.76 (dm, *J* 254.3, P(C$_6$F$_5$)), 142.50 (dm, *J* 257.2, P(C$_6$F$_5$)), 147.96 (dm, *J* 246.6, P(C$_6$F$_5$)); δ_P (121 MHz; C$_6$D$_6$): −50.47 (quin, *J* 22.2, P(C$_6$F$_5$)), 49.38 (br, PBu^t); δ_F (282 MHz; C$_6$D$_6$): −160.32 (4F, m, P(*m*-C$_6$F$_5$)), −149.37 (2F, tt, *J* 21.8, 4.0, P(*p*-C$_6$F$_5$)), −130.11 (4F, m, P(*o*-C$_6$F$_5$)). HRMS found: *m/z* 627.1597; calc. for C$_{28}$H$_{28}$BF$_{10}$P$_2$ [M−H]$^+$: 627.1599.

General procedure for synthesis of α-(di-*t*-butylphosphino)-α′-thio-*o*-xylene–borane compounds (7) Sodium metal (0.164 g, 7.1 mmol) and ethanol (50 mL) were combined and after reaction was complete, the appropriate thiol (7.5 mmol) was added and resulting solution stirred for 1 h. Compound **1** (1.05 g, 3.5 mmol) was added and the mixture stirred overnight, followed by solvent evaporation under reduced pressure. The resulting white solid was dissolved in toluene (50 mL) in the air, filtered and the solvent evaporated under reduced pressure leaving crude product, which was recrystallised from *n*-hexane.

*α-(Di-t-butylphosphino)-α′-(t-butylthio)-o-xylene–borane (**7a**)* White powdery crystals (0.98 g, 80%). Anal. found: C, 68.0; H, 11.1; S, 9.0; calc. for C$_{20}$H$_{38}$BPS: C, 68.2; H, 10.9; S, 9.1%. IR ν_{max}/cm^{-1}: 2383 (BH), 2902–3051 (CH). NMR δ_H (500 MHz; C$_6$D$_6$): 1.0–1.8 (3H, br, BH$_3$), 1.12 (18H, d, *J* 12.5, PBu^t), 1.29 (9H, s, SBu^t), 3.27 (2H, d, *J* 12.0, CH$_2$P), 3.99 (2H, s, CH$_2$S), 6.99 (1H, t, *J* 7.5, Ar), 7.04 (1H, t, *J* 7.5, Ar), 7.23 (1H, d, *J* 7.0, Ar), 7.79 (1H, d, *J* 8.0, Ar); δ_C (125 MHz; C$_6$D$_6$): 22.43 (d, *J* 23.5, CH$_2$P), 28.38 (d, *J* 1.0, PC*Me*$_3$), 30.98 (s, SC*Me*$_3$), 32.93 (s, CH$_2$S), 33.08 (d, *J* 24.8, P*C*Me$_3$), 42.67 (s, S*C*Me$_3$), 127.22 (d, *J* 1.5, Ar), 127.37 (d, *J* 1.9, Ar), 131.69 (d, *J* 1.4, Ar), 132.16 (d, *J* 3.3, Ar), 134.67 (d, *J* 3.4, Ar), 137.17 (d, *J* 4.8, Ar); δ_P (121 MHz; C$_6$D$_6$): 47.94 (br); δ_B (96 MHz; C$_6$D$_6$): −40.37 (d, *J* 47.6). HRMS found: *m/z* 374.2462; calc. for C$_{20}$H$_{38}$BNaPS [M+Na]$^+$: 374.2459.

*α-(Di-t-butylphosphino)-α′-(phenylthio)-o-xylene–borane (**7b**)* White plate-like crystals (0.98 g, 75%). Anal. found: C, 71.0; H, 9.4; S, 8.5; calc. for C$_{22}$H$_{34}$BPS: C, 71.0; H, 9.2; S, 8.6%. IR ν_{max}/cm^{-1}: 2381 (BH), 2870–3059 (CH). NMR δ_H (500 MHz; C$_6$D$_6$): 0.9–1.7 (3H, br, BH$_3$), 1.05 (18H, d, *J* 12.0, PBu^t), 3.20 (2H, d, *J* 12.0, CH$_2$P), 4.40 (2H, s, CH$_2$S), 6.92 (2H, m, Ar & SPh), 7.01 (4H, m, Ar & SPh), 7.32 (2H, d, *J* 8.5, SPh), 7.61 (1H, d, *J* 8.0, Ar); δ_C (125 MHz; C$_6$D$_6$): 22.31 (d, *J* 22.9, CH$_2$P), 28.31 (d, *J* 1.0, PC*Me*$_3$), 32.99 (d, *J* 24.4, P*C*Me$_3$), 38.50 (s, CH$_2$S), 126.52 (s, SPh), 127.33 (d, *J* 2.0, Ar), 127.51 (d, *J* 1.4, Ar), 129.17 (s, SPh), 130.11 (s, SPh), 131.57 (d, *J* 1.5, Ar), 132.20 (d, *J* 3.4, Ar), 134.67 (d, *J* 3.4, Ar), 136.61 (d, *J* 4.3, Ar), 137.21 (s, SPh); δ_P (121 MHz; C$_6$D$_6$): 47.97 (br); δ_B (96 MHz; C$_6$D$_6$): −40.65 (d, *J* 48.4). HRMS found: *m/z* 395.2116; calc. for C$_{22}$H$_{34}$BNaPS [M+Na]$^+$: 395.2110.

α-(Di-*t*-butylphosphino)-α′-(*t*-butylsulfinyl)-*o*-xylene–borane (8) Compound **7a** (1.00 g, 2.84 mmol), 3-carboxypyridinium chlorochromate (0.74 g, 2.84 mmol) and aluminium trichloride (0.38 g, 2.84 mmol) were combined in acetonitrile (50 mL) in the air, and heated to reflux for 2 h. The resulting mixture was separated by centrifugation and the solid washed with acetonitrile (2 × 40 mL). The combined purple solutions were passed through a plug of alumina, which was then washed through with further acetonitrile (30 mL). Solvent evaporation under reduced pressure gave the crude product. Recrystallisation from hot toluene gave desired compound **7a**. Hygroscopic white powder (0.61 g, 58%). Anal. found: C, 65.1; H, 10.6; S, 8.4; calc. for C$_{20}$H$_{38}$BOPS: C, 65.2; H, 10.4; S, 8.7%. IR ν_{max}/cm^{-1}: 1028 (SO), 2391 (BH), 2870–3052 (CH). NMR δ_H (500 MHz; C$_6$D$_6$): 0.8–1.6 (3H, br, BH$_3$), 1.06 (9H, d, *J* 12.5, PBu^t), 1.09 (9H, s, SBu^t), 1.19 (9H, d, *J* 12.5, PBu^t), 3.04 (1H, t, *J* 15.0, CH$_2$P), 3.63 (1H, d, *J* 13.5, CH$_2$S), 4.07 (1H, dd, *J* 15.0, 9.0, CH$_2$P), 4.61 (1H, d, *J* 13.5, CH$_2$S), 7.06 (3H, m, Ar), 7.36 (1H, d, *J* 7.5, Ar); δ_C (150 MHz; C$_6$D$_6$): 22.95 (s, SC*Me*$_3$), 23.33 (d, *J* 22.7, CH$_2$P), 28.51 (d, *J* 0.9, PC*Me*$_3$), 28.53 (d, *J* 1.1, PC*Me*$_3$), 32.99 (d, *J* 25.0, P*C*Me$_3$), 33.01 (d, *J* 24.1, P*C*Me$_3$), 52.19 (d, *J* 1.2, CH$_2$S), 53.44 (s, S*C*Me$_3$), 127.43 (d, *J* 2.0, Ar), 127.55 (d, *J* 2.2, Ar), 132.39 (d, *J* 2.0, Ar), 132.56 (d, *J* 3.9, Ar), 134.34 (d, *J* 3.6, Ar), 136.47 (d, *J* 3.9, Ar); δ_P (121 MHz; C$_6$D$_6$): 47.98 (br). HRMS found: *m/z* 391.2376; calc. for C$_{20}$H$_{38}$BNaOPS [M+Na]$^+$: 391.2372.

General procedure for synthesis of α-(di-*t*-butylphosphino)-α′-(dialkylamino)-*o*-xylene–diborane compounds (11) A solution of dialkylamine–borane (1.6 mmol) in THF (5 mL) was cooled to 0 °C and a solution of *n*-butyllithium (1.0 mL, 1.6 M in hexanes, 1.6 mmol) was added dropwise with stirring. The mixture was stirred at room temperature for 1 h, then added dropwise to a solution of **1** (0.42 g, 1.4 mmol) in THF (5 mL) at −5 °C and stirred at this temperature for 1 h. The solvent was evaporated under reduced pressure, and the resulting white solid was stirred in distilled water (10 mL) in the air for 1 h, filtered and recrystallised from 1:2 toluene/*n*-hexane.

*α-(Di-t-butylphosphino)-α′-(dimethylamino)-o-xylene–diborane (**11a**)* White needle-like crystals (0.36 g, 80%). Anal. found: C, 67.4; H, 12.1; N, 4.4; calc. for C$_{18}$H$_{38}$B$_2$NP:

C, 67.3; H, 11.9; N, 4.4%. IR ν_{max}/cm^{-1}: 2278–2380 (BH), 2871–2988 (CH). NMR δ_H (500 MHz; C_6D_6): 0.8–1.6 (3H, br, PBH_3), 1.08 (18H, d, *J* 12.0, PBu^t), 1.9–2.8 (3H, br, NBH_3), 2.09 (3H, s, NMe), 3.55 (2H, d, *J* 12.0, CH_2P), 3.98 (2H, s, CH_2N), 6.74 (1H, d, *J* 8.0, Ar), 6.93 (1H, t, *J* 7.5, Ar), 7.09 (1H, t, *J* 7.5, Ar), 7.69 (1H, d, *J* 8.0, Ar); δ_C (125 MHz; C_6D_6): 24.08 (d, *J* 22.5, CH_2P), 28.43 (d, *J* 1.0, $PCMe_3$), 32.99 (d, *J* 24.4, $PCMe_3$), 51.32 (s, NMe), 64.98 (s, CH_2N), 126.23 (d, *J* 2.4, Ar), 128.62 (d, *J* 2.0, Ar), 132.02 (d, *J* 4.3, Ar), 132.74 (d, *J* 3.8, Ar), 133.51 (d, *J* 1.4, Ar), 137.70 (d, *J* 3.8, Ar); δ_P (121 MHz; C_6D_6): 49.80 (br); δ_B (96 MHz; C_6D_6): −40.83 (d, *J* 52.5, PBH_3), −8.78 (s, NBH_3). HRMS found: *m/z* 344.2832; calc. for $C_{18}H_{38}B_2NNaP$ $[M+Na]^+$: 344.2832.

α-(Di-t-butylphosphino)-α′-pyrrolidino-o-xylene–diborane ***(11b)*** White needle-like crystals (0.43 g, 89%). Anal. found: C, 69.1; H, 11.7; N, 4.0; calc. for $C_{20}H_{40}B_2NP$: C, 69.2; H, 11.6; N, 4.0%. IR ν_{max}/cm^{-1}: 2279–2379 (BH), 2904–3052 (CH). NMR δ_H (500 MHz; C_6D_6): 0.8–1.6 (3H, br, PBH_3), 1.13 (18H, d, *J* 12.5, PBu^t), 1.8–2.6 (3H, br, NBH_3), 1.19 (2H, m, NCH_2CH_2), 1.82 (2H, m, NCH_2CH_2), 2.31 (2H, m, NCH_2CH_2), 2.90 (2H, m, NCH_2CH_2), 3.69 (2H, d, *J* 12.0, CH_2P), 4.10 (2H, s, $ArCH_2N$), 6.84 (1H, d, *J* 7.5, Ar), 6.99 (1H, t, *J* 7.5, Ar), 7.11 (1H, t, *J* 7.5, Ar), 7.66 (1H, d, *J* 7.5, Ar); δ_C (125 MHz; C_6D_6): 22.15 (s, NCH_2CH_2), 24.36 (d, *J* 22.9, CH_2P), 28.50 (d, *J* 1.0, $PCMe_3$), 33.06 (d, *J* 24.4, $PCMe_3$), 59.93 (s, NCH_2CH_2), 63.18 (s, $ArCH_2N$), 126.39 (d, *J* 2.4, Ar), 132.71 (d, *J* 3.4, Ar), 132.79 (d, *J* 1.9, Ar), 133.28 (d, *J* 3.8, Ar), 138.00 (d, *J* 3.9, Ar), other Ar obscured by solvent; δ_P (121 MHz; C_6D_6): 49.55 (br); δ_B (96 MHz; C_6D_6): −40.86 (d, *J* 47.8, PBH_3), −11.44 (s, NBH_3). HRMS found: *m/z* 370.2981; calc. for $C_{20}H_{40}B_2NNaP$ $[M+Na]^+$: 370.2990.

α-(Di-t-butylphosphino)-α′-(diethylamino)-o-xylene–diborane ***(11c)*** White crystals (0.39 g, 80%). Anal. found: C, 68.9; H, 12.2; N, 3.9; calc. for $C_{20}H_{42}B_2NP$: C, 68.8; H, 12.1; N, 4.0%. IR ν_{max}/cm^{-1}: 2281–2366 (BH), 2872–2998 (CH). NMR δ_H (500 MHz; C_6D_6): 0.6–1.6 (3H, br, PBH_3), 0.88 (6H, t, *J* 7.0, NCH_2Me), 1.12 (18H, d, *J* 12.5, PBu^t), 1.6–2.5 (3H, br, NBH_3), 2.50 (2H, sext, *J* 7.0, NCH_2Me), 2.62 (2H, sext, *J* 7.0, NCH_2Me), 3.82 (2H, d, *J* 12.0, CH_2P), 4.02 (2H, s, $ArCH_2N$), 6.95 (1H, d, *J* 7.5, Ar), 7.00 (1H, t, *J* 7.5, Ar), 7.10 (1H, t, *J* 7.5, Ar), 7.53 (1H, d, *J* 7.5, Ar); δ_C (125 MHz; C_6D_6): 8.75 (s, NCH_2Me), 24.75 (d, *J* 22.5, CH_2P), 28.55 (s, $PCMe_3$), 33.01 (d, *J* 24.8, $PCMe_3$), 52.51 (s, NCH_2Me), 60.35 (s, $ArCH_2N$), 126.08 (d, *J* 2.4, Ar), 132.89 (d, *J* 3.8, Ar), 133.07 (d, *J* 3.8, Ar), 133.18 (d, *J* 1.9, Ar), 138.35 (d, *J* 3.8, Ar), other Ar obscured by solvent; δ_P (121 MHz; C_6D_6): 49.80 (br); δ_B (96 MHz; C_6D_6): −40.97 (d, *J* 53.7, PBH_3), −12.93 (s, NBH_3). HRMS found: *m/z* 372.3138; calc. for $C_{20}H_{42}B_2NNaP$ $[M+Na]^+$: 372.3146.

α-(Di-*t*-butylphosphino)-α′-(diphenylsilyl)-*o*-xylene–borane (13) Flame-dried magnesium turnings (24 mg, 1.00 mmol), compound **1** (150 mg, 0.50 mmol), chlorodiphenylsilane (0.15 mL, 0.75 mmol), a crystal of iodine and THF (12 mL) were combined and stirred at room temperature overnight. The solvent was removed under reduced pressure, the resulting mixture extracted into toluene (15 mL) in the air, filtered and solvent again removed under reduced pressure. Elution through an alumina column with 1% ethyl acetate in *n*-hexane gave pure compound **13** (R_f = 0.33). Air-stable clear oil (75 mg, 34%). Anal. found: C, 75.3; H, 9.2; calc. for $C_{28}H_{40}BPSi$: C, 75.3; H, 9.0%. NMR δ_H (500 MHz; C_6D_6): 1.0–1.8 (3H, br, BH_3), 1.03 (18H, d, *J* 12.2, PBu^t), 2.69 (2H, d, *J* 12.0, CH_2P), 2.93 (2H, d, *J* 3.4, CH_2Si), 5.10 (1H, t, *J* 3.1, $^1J_{SiH}$ 197.3, SiH), 6.97 (3H, m, Ar), 7.11 (6H, m, SiPh), 7.45 (4H, d, *J* 7.6, SiPh), 7.82 (1H, d, *J* 7.8, Ar); δ_C (125 MHz; C_6D_6): 21.71 (s, CH_2Si), 22.91 (d, *J* 23.1, CH_2P), 28.34 (s, $PCMe_3$), 32.97 (d, *J* 23.9, $PCMe_3$), 125.20 (d, *J* 1.9, Ar), 127.22 (d, *J* 1.9, Ar), 128.39 (s, SiPh), 130.19 (s, SiPh), 130.59 (d, *J* 1.5, Ar), 132.12 (d, *J* 2.9, Ar), 132.98 (d, *J* 3.3, Ar), 133.73 (s, SiPh), 135.67 (s, SiPh), 137.60 (d, *J* 4.8, Ar); δ_P (121 MHz; C_6D_6): 48.57 (br). HRMS found: *m/z* 445.2643; calc. for $C_{28}H_{39}BPSi$ $[M-H]^+$: 445.2652.

General procedure for deprotection of compounds 2, 7 and 8, and synthesis of compound 6 The appropriate phosphine–borane (50 mg) and morpholine (1 mL) were combined in a sealed tube and heated to 100 °C for 1 h. After cooling, the solvent was evaporated under reduced pressure. The resulting white solid was extracted with *n*-hexane (2 × 2 mL), filtered through a plug of alumina, and the solvent evaporated under reduced pressure, giving desired product.

α-(Di-t-butylphosphino)-α′-(diphenylphosphino)-o-xylene ***(3)*** Highly air-sensitive white solid (39 mg, 82%). NMR δ_H (500 MHz; C_6D_6): 1.09 (18H, d, *J* 10.5, PBu^t), 3.09 (2H, s, CH_2PBu^t), 3.92 (2H, d, *J* 2.5, CH_2PPh), 6.75 (1H, d, *J* 7.6, Ar), 6.85 (1H, t, *J* 7.5, Ar), 7.00 (1H, t, *J* 7.6, Ar), 7.04 (6H, m, PPh), 7.42 (4H, m, PPh), 7.50 (1H, d, *J* 7.9, Ar); δ_C (125 MHz; C_6D_6): 27.41 (dd, *J* 26.9, 6.7, CH_2PBu^t), 30.10 (d, *J* 13.4, $PCMe_3$), 32.12 (d, *J* 24.0, $PCMe_3$), 34.63 (dd, *J* 17.0, 11.8, CH_2PPh), 125.82 (t, *J* 1.9, Ar), 126.28 (d, *J* 2.9, Ar), 128.59 (d, *J* 6.2, PPh), 128.77 (s, PPh), 131.45 (d, *J* 7.2, Ar), 131.74 (dd, *J* 10.6, 1.4, Ar), 133.51 (d, *J* 18.2, PPh), 136.03 (dd, *J* 6.5, 2.2, Ar), 139.28 (d, *J* 16.3, PPh), 139.60 (dd, *J* 8.7, 3.9, Ar); δ_P (121 MHz; C_6D_6): −15.61 (d, *J* 1.4, PPh), 24.47 (d, *J* 1.4, PBu^t).

α-(Di-t-butylphosphino)-α′-{bis(p-N-morpholinotetrafluorophenyl)phosphino}-o-xylene ***(6)*** Highly air-sensitive white expanded oil (50 mg, 84%). NMR δ_H (500 MHz; C_6D_6): 1.12 (18H, d, *J* 10.7, PBu^t), 2.76 (8H, br s, CH_2N), 3.20 (2H, s, CH_2PBu^t), 3.36 (8H, br s, CH_2O), 4.53 (2H, s,

$CH_2P(C_6F_4)N$), 6.85 (1H, t, *J* 7.3, Ar), 6.98 (2H, m, Ar), 7.56 (1H, d, *J* 7.0, Ar); δ_C (125 MHz; C_6D_6): 27.11 (dd, *J* 27.3, 7.2, CH_2PBu^t), 29.78 (m, $CH_2P(C_6F_4)N$), 30.00 (d, *J* 13.4, $PCMe_3$), 32.11 (d, *J* 24.5, $PCMe_3$), 51.11 (t, *J* 3.4, CH_2N), 67.05 (s, CH_2O), 106.06 (m, $P(C_6F_4)N$), 126.13 (s, Ar), 127.24 (d, *J* 3.4, Ar), 130.83 (d, *J* 8.7, Ar), 132.00 (m, $P(C_6F_4)N$), 132.19 (dd, *J* 12.5, 2.4, Ar), 134.37 (dd, *J* 7.8, 2.1, Ar), 140.12 (dd, *J* 9.1, 4.3, Ar), 142.06 (dm, *J* 230.3, $P(C_6F_4)N$), 149.04 (dm, *J* 234.2, $P(C_6F_4)N$); δ_P (121 MHz; C_6D_6): −51.73 (quind, *J* 23.7, 8.1, $P(C_6F_4)N$), 25.40 (d, *J* 8.1, PBu^t); δ_F (282 MHz; C_6D_6): −150.56 (4F, dd, *J* 20.9, 7.0, P(*m*-C_6F_4)N), −132.47 (4F, td, *J* 22.8, 9.9, P(*o*-C_6F_4)N). HRMS found: *m/z* 749.2659; calc. for $C_{36}H_{43}F_8N_2O_2P_2$ $[M+H]^+$: 749.2667.

α-(Di-t-butylphosphino)-α′-(t-butylthio)-o-xylene ***(9a)*** Highly air-sensitive clear oil (44 mg, 92%). NMR δ_H (600 MHz; C_6D_6): 1.13 (18H, d, *J* 10.6, PBu^t), 1.29 (9H, s, SBu^t), 3.09 (2H, d, *J* 1.2, CH_2P), 4.05 (2H, s, CH_2S), 7.01 (1H, t, *J* 7.3, Ar), 7.07 (1H, t, *J* 7.7, Ar), 7.31 (1H, d, *J* 7.3, Ar), 7.68 (1H, d, *J* 7.3, Ar); δ_C (150 MHz; C_6D_6): 26.21 (d, *J* 26.0, CH_2P), 30.07 (d, *J* 13.2, $PCMe_3$), 31.00 (s, $SCMe_3$), 32.01 (d, *J* 24.2, $PCMe_3$), 32.25 (d, *J* 8.7, CH_2S), 42.57 (s, $SCMe_3$), 126.18 (d, *J* 1.8, Ar), 127.20 (s, Ar), 131.14 (s, Ar), 131.63 (d, *J* 14.4, Ar), 136.58 (d, *J* 2.9, Ar), 140.06 (d, *J* 9.2, Ar); δ_P (121 MHz; C_6D_6): 24.99 (s).

α-(Di-t-butylphosphino)-α′-(phenylthio)-o-xylene ***(9b)*** Highly air-sensitive white solid (33 mg, 69%). NMR δ_H (500 MHz; C_6D_6): 1.07 (18H, d, *J* 10.8, PBu^t), 3.06 (2H, s, CH_2P), 4.51 (2H, d, *J* 2.2, CH_2S), 6.93 (2H, m, Ar & SPh), 6.99 (2H, t, *J* 7.6, SPh), 7.03 (1H, t, *J* 7.3, Ar), 7.09 (1H, d, *J* 7.5, Ar), 7.30 (2H, d, *J* 7.0, SPh), 7.47 (1H, d, *J* 7.5, Ar); δ_C (125 MHz; C_6D_6): 26.79 (d, *J* 27.4, CH_2P), 29.99 (d, *J* 13.5, $PCMe_3$), 32.04 (d, *J* 24.4, $PCMe_3$), 37.84 (d, *J* 12.9, CH_2S), 126.19 (d, *J* 1.4, Ar), 126.35 (s, SPh), 127.57 (s, Ar), 129.06 (s, SPh), 130.23 (s, SPh), 131.18 (s, Ar), 131.91 (d, *J* 10.5, Ar), 135.65 (d, *J* 2.4, Ar), 137.50 (s, SPh), 140.16 (d, *J* 8.6, Ar); δ_P (121 MHz; C_6D_6): 25.93 (s).

α-(Di-t-butylphosphino)-α′-(t-butylsulfinyl)-o-xylene ***(10)*** Highly air-sensitive white solid (39 mg, 81%). NMR δ_H (500 MHz; C_6D_6): 1.06 (9H, d, *J* 10.9, PBu^t), 1.08 (9H, s, SBu^t), 1.14 (9H, d, *J* 10.8, PBu^t), 2.99 (1H, dd, *J* 14.8, 2.0, CH_2P), 3.37 (1H, d, *J* 14.9, CH_2P), 3.85 (1H, dd, *J* 13.0, 1.4, CH_2S), 4.25 (1H, dd, *J* 13.0, 3.5, CH_2S), 7.04 (2H, m, Ar), 7.23 (1H, d, *J* 8.1, Ar), 7.46 (1H, d, *J* 7.1, Ar); δ_C (125 MHz; C_6D_6): 22.99 (s, $SCMe_3$), 27.59 (d, *J* 26.4, CH_2P), 30.06 (d, *J* 13.0, $PCMe_3$), 30.13 (d, *J* 13.0, $PCMe_3$), 32.04 (d, *J* 26.9, $PCMe_3$), 32.22 (d, *J* 26.4, $PCMe_3$), 50.89 (d, *J* 13.4, CH_2S), 53.46 (s, $SCMe_3$), 126.41 (d, *J* 1.5, Ar), 128.00 (s, Ar), 131.79 (d, *J* 1.9, Ar), 132.04 (d, *J* 10.5, Ar), 132.54 (s, Ar), 141.00 (d, *J* 7.7, Ar); δ_P (121 MHz; C_6D_6): 25.23 (s).

General procedure for deprotection of compounds 4 and 11 A solution of the appropriate phosphine–borane (0.14 mmol) in dichloromethane (3 mL) was cooled to −10 °C, tetrafluoroboric acid–diethyl ether complex (0.24 mL, 85% solution, 1.4 mmol) added dropwise, and the resulting solution stirred at room temperature for 1 h. Diethyl ether (4 mL) was added, followed by saturated sodium hydrogen carbonate solution (8 mL), and the mixture stirred for 30 min. The resulting layers were separated, the aqueous layer washed with diethyl ether (2 × 4 mL), combined organic fractions washed with distilled water (4 mL) and brine (4 mL), and solvent evaporated under reduced pressure. The resulting material was extracted into *n*-hexane (6 mL), dried over magnesium sulfate and filtered through a plug of alumina. The solvent was evaporated under reduced pressure, giving desired product.

α-(Di-t-butylphosphino)-α′-{bis(pentafluorophenyl)phosphino}-o-xylene ***(5)*** Highly air-sensitive white solid (44 mg, 51%). NMR δ_H (500 MHz; C_6D_6): 1.07 (18H, d, *J* 10.8, PBu^t), 3.07 (2H, s, CH_2PBu^t), 4.27 (2H, s, $CH_2P(C_6F_5)$), 6.69 (1H, d, *J* 7.8, Ar), 6.74 (1H, t, *J* 7.3, Ar), 6.91 (1H, t, *J* 7.5, Ar), 7.41 (1H, d, *J* 7.6, Ar); δ_C (125 MHz; C_6D_6): 27.36 (dd, *J* 27.8, 6.7, CH_2PBu^t), 29.29 (m, $CH_2P(C_6F_5)$), 29.87 (d, *J* 13.4, $PCMe_3$), 32.07 (d, *J* 24.0, $PCMe_3$), 109.13 (m, $P(C_6F_5)$), 126.24 (dd, *J* 2.4, 1.9, Ar), 127.63 (d, *J* 3.4, Ar), 130.50 (d, *J* 9.6, Ar), 132.36 (dd, *J* 11.1, 2.4, Ar), 133.21 (dd, *J* 7.7, 1.9, Ar), 137.77 (dm, *J* 252.9, $P(C_6F_5)$), 139.97 (dd, *J* 8.6, 4.3, Ar), 142.46 (dm, *J* 257.2, $P(C_6F_5)$), 148.03 (dm, *J* 246.6, $P(C_6F_5)$); δ_P (121 MHz; C_6D_6): −50.87 (quind, *J* 22.3, 11.9, $P(C_6F_5)$), 25.15 (d, *J* 12.6, PBu^t); δ_F (282 MHz; C_6D_6): −160.51 (4F, m, P(*m*-C_6F_5)), −149.81 (2F, tt, *J* 20.8, 4.0, P(*p*-C_6F_5)), −130.01 (4F, m, P(*o*-C_6F_5)).

α-(di-t-butylphosphino)-α′-(dimethylamino)-o-xylene ***(12a)*** Highly air-sensitive cloudy oil (35 mg, 85%). NMR δ_H (500 MHz; C_6D_6): 1.13 (18H, d, *J* 10.7, PBu^t), 2.11 (6H, s, NMe), 3.16 (2H, d, *J* 2.4, CH_2P), 3.60 (2H, s, CH_2N), 7.05 (1H, t, *J* 7.3, Ar), 7.15 (1H, t, *J* 7.6, Ar), 7.21 (1H, d, *J* 7.3, Ar), 7.77 (1H, d, *J* 7.3, Ar); δ_C (125 MHz; C_6D_6): 25.53 (d, *J* 25.5, CH_2P), 30.02 (d, *J* 13.9, $PCMe_3$), 31.95 (d, *J* 24.0, $PCMe_3$), 45.46 (s, NMe), 63.46 (d, *J* 6.2, CH_2N), 125.56 (d, *J* 1.9, Ar), 127.38 (s, Ar), 131.08 (s, Ar), 131.54 (d, *J* 14.8, Ar), 137.54 (d, *J* 2.9, Ar), 141.20 (d, *J* 10.1, Ar); δ_P (121 MHz; C_6D_6): 24.53 (s).

α-(di-t-butylphosphino)-α′-pyrrolidino-o-xylene ***(12b)*** Highly air-sensitive clear oil (27 mg, 60%). NMR δ_H (500 MHz; C_6D_6): 1.14 (18H, d, *J* 10.5, PBu^t), 1.58 (4H, m, NCH_2CH_2), 2.40 (4H, m, NCH_2CH_2), 3.16 (2H, d, *J* 2.7, CH_2P), 3.82 (2H, s, $ArCH_2N$), 7.07 (1H, t, *J* 7.3, Ar), 7.16 (1H, t, *J* 7.6, Ar), 7.27 (1H, d, *J* 7.5, Ar), 7.81 (1H, dd, *J* 7.6, 1.5, Ar); δ_C (125 MHz; C_6D_6): 23.90 (s, NCH_2CH_2), 25.29 (d, *J* 25.0, CH_2P), 30.00 (d, *J* 13.4, $PCMe_3$), 31.95 (d, *J* 24.0,

P*C*Me$_3$), 54.31 (s, NCH$_2$CH$_2$), 59.64 (d, *J* 5.8, ArCH$_2$N), 125.60 (d, *J* 1.9, Ar), 127.24 (s, Ar), 130.50 (s, Ar), 131.35 (d, *J* 15.4, Ar), 138.15 (d, *J* 2.9, Ar), 140.87 (d, *J* 10.5, Ar); δ_P (121 MHz; C_6D_6): 24.56 (s).

α-(di-t-butylphosphino)-α′-(diethylamino)-o-xylene ***(12c)*** Highly air-sensitive clear oil (33 mg, 73%). NMR δ_H (500 MHz; C_6D_6): 0.97 (6H, t, *J* 7.1, NCH$_2$*Me*), 1.14 (18H, d, *J* 10.8, PBu^t), 2.46 (4H, q, *J* 7.1, NC*H*$_2$Me), 3.12 (2H, d, *J* 2.7, CH$_2$P), 3.69 (2H, s, ArCH$_2$N), 7.08 (1H, t, *J* 7.3, Ar), 7.17 (1H, t, *J* 7.4, Ar), 7.33 (1H, d, *J* 7.3, Ar), 7.95 (1H, dd, *J* 7.3, 2.9, Ar); δ_C (125 MHz; C_6D_6): 11.81 (s, NCH$_2$*Me*), 25.17 (d, *J* 24.0, CH$_2$P), 30.09 (d, *J* 13.5, P*C*Me$_3$), 32.00 (d, *J* 24.0, P*C*Me$_3$), 46.89 (s, N*C*H$_2$Me), 57.64 (d, *J* 3.9, ArCH$_2$N), 125.55 (d, *J* 1.9, Ar), 127.16 (s, Ar), 130.88 (s, Ar), 131.26 (d, *J* 18.2, Ar), 138.00 (d, *J* 3.3, Ar), 140.96 (d, *J* 11.0, Ar); δ_P (121 MHz; C_6D_6): 23.76 (s).

α-(Di-*t*-butylphosphino)-α′-(diphenylsilyl)-*o*-xylene (14) Compound **13** (15 mg, 0.03 mmol) and DABCO (4 mg, 0.04 mmol) were combined in toluene (0.5 mL) and heated to 60 °C overnight. After cooling, the solvent was evaporated under reduced pressure. The resulting white solid was extracted with *n*-hexane (2 × 1 mL), filtered through a plug of alumina, and the solvent evaporated under reduced pressure, giving desired product **14**. Highly air-sensitive white solid (9 mg, 69%). NMR δ_H (500 MHz; C_6D_6): 1.05 (18H, d, *J* 10.5, PBu^t), 2.65 (2H, d, *J* 1.5, CH$_2$P), 3.10 (2H, dd, *J* 3.4, 1.5, CH$_2$Si), 5.22 (1H, t, *J* 3.7, $^1J_{SiH}$ 197.5, SiH), 6.95 (1H, m, Ar), 7.01 (2H, m, Ar), 7.13 (6H, m, SiPh), 7.51 (4H, dd, *J* 7.5, 1.2, SiPh), 7.53 (1H, d, *J* 7.8, Ar); δ_C (125 MHz; C_6D_6): 20.72 (d, *J* 8.6, CH$_2$Si), 27.17 (d, *J* 26.4, CH$_2$P), 30.03 (d, *J* 13.5, PC*Me*$_3$), 31.97 (d, *J* 25.0, P*C*Me$_3$), 125.13 (s, Ar), 126.07 (d, *J* 2.0, Ar), 128.29 (s, SiPh), 130.01 (s, SiPh), 130.44 (s, Ar), 131.71 (d, *J* 12.5, Ar), 134.23 (s, SiPh), 135.76 (s, SiPh), 137.33 (d, *J* 2.4, Ar), 138.45 (d, *J* 8.6, Ar); δ_P (121 MHz; C_6D_6): 25.22 (s).

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