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Palladium-catalysed synthesis of biaryl phosphines

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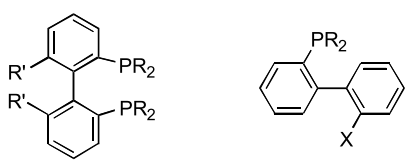
Abstract—Monodentate, biphenyl-type phosphines have emerged as a powerful class of ligands in homogeneous catalysis. Synthetic methods for these ligands are limited, however. We report that the palladium-catalysed Suzuki coupling of $OPR_2(o\text{-}C_6H_4X)$ (R=Ph, *t*-Bu; X=Br, I) with arylboronic acids affords a variety of biaryl phosphine oxides including those that contain heterocycles. The corresponding phosphines are readily obtained by treatment with $HSiCl_3$. The methodology provides an easy entry to monodentate biaryl and heterobiaryl P^X (X=N, O, S) phosphines with diverse steric and electronic properties.

1. Introduction

Phosphines play an extremely important role in homogeneous catalysis, with the choice of ligand often being the crucial factor in determining the success of a reaction.[1] In particular, those possessing novel electronic and steric properties and functional groups are of extra interest, as they can have beneficial effects for metal-catalysed reactions in a homogeneous or multi-phasic solution or on solid surfaces.[1] A class of ligand worthy of note is those containing *ortho*-substituted biphenyl backbones, which can be distinguished into two groups, mono- and bis-phosphines (Scheme 1). Of the latter, 2,2′-bis(diphenylphosphino)biphenyl (BIPHEP) and its derivatives are probably the best known, although their chemistry have not been extensively explored.[2] Hayashi has shown that BIPHEP is an excellent ligand for C–C and C–N bond formation.[2b,c] In an interesting development by Mikami, the dynamic axial chirality of BIPHEP ligands has been successfully exploited in asymmetric transformations through asymmetric activation.[2a,d] Several chiral derivatives of BIPHEP are known and have been used in a number of asymmetric reactions, including asymmetric hydrogenation.[2g]



Scheme 1.

The monodentate analogues of BIPHEP-type ligands have only recently emerged as powerful ligands. Although they have found success in metal-catalysed reactions such as hydroformylation[3] and asymmetric allylic alkylation,[4] they have shown to be most outstanding in palladium-catalysed C–X bond forming reactions, including Suzuki coupling, arylation of enolates, Hiyama reaction, aromatic amination, and etherisation.[5] These phosphines represent some of the most effective ligands identified so far for C–X bond formation.[6] The effectiveness of the ligands is attributed to two factors; they are electron-rich and sterically crowded. It is generally accepted that the former factor facilitates oxidative addition whilst the latter can be expected to enhance reductive elimination. *t*-Butyl and cyclohexyl spectator groups at phosphorus have been used to provide electron density, whilst both the spectator group and the biphenyl unit provide the steric bulk. However, the biphenyl group may be more significant in the effectiveness of these ligands than first realised and may provide the key to their success. They could shield and stabilise palladium from coordination to further ligands through steric as well as electronic interactions, thus providing a highly active monophosphine–palladium catalyst.[7] Very recently, an X-ray study of the structure of $[PdL_2]$ [L=2-(dicyclohexylphosphino)biphenyl] has indeed revealed an unusual η^1-coordination of one of the biphenyl rings to Pd(0).[7d] Additionally, when donor substituents are present, possible hemilabile coordination to palladium could provide further stabilisation in the catalyst resting state, thereby increasing catalyst lifetime.

The monodentate biphenyl phosphines are most often prepared using Grignard and lithium reagents.[3–5] More recently, Buchwald has developed an improved synthesis for alkylphosphinobiphenyl ligands, where aryl magnesium halides are reacted with benzyne, followed by addition of a

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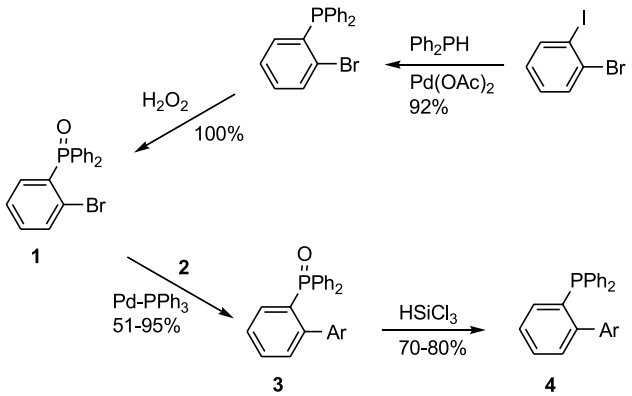
chlorodialkylphosphine.[8] Following an initial report,[9] we describe herein an alternative methodology for the synthesis of biphenyl-based phosphines, which utilises the palladium-catalysed Suzuki reaction. By constructing the biphenyl component in this manner, we could potentially generate ligands with varying steric and electronic properties due to the increased commercial availability of arylboronic acids and the increased functional group tolerance of the Suzuki reaction compared with more traditional methods. The methodology could also be easily extended to incorporate various biaryl groups, giving rise to novel hemilabile phosphine ligands P^X (X=N, O, S) that may find use in coordination chemistry and catalysis.[10] Suzuki coupling has been employed in phosphine synthesis in only a few instances.[11] Of relevance to this study is that of Buchwald, in which arylboronic acids are asymmetrically coupled with a bromonaphthylphosphonate in high yields and excellent ee values.[11b] To our knowledge, however, this simple method has not been applied to the synthesis of biaryl- or heterobiaryl-phosphines to be described herein.

2. Results and discussion

We have recently reported the catalytic synthesis of aryl-phosphines applicable to catalysis in solvents of widely differing solubility properties.[12] The approach utilised a common haloarylphosphine oxide $OPPh_{3-n}(p\text{-}C_6H_4Br)_n$ as a starting block. Using a similar approach but starting with the *ortho*-brominated $OPPh_2(o\text{-}C_6H_4Br)$ **1**, various biphenyl phosphines and related ligands could be easily envisioned through Suzuki coupling with aryl boronic acids **2** (Scheme 2).



Scheme 2.

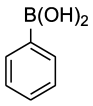
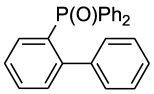
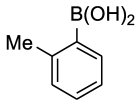
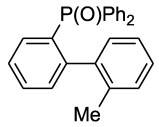
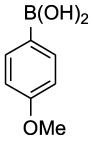
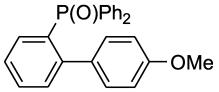
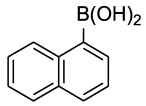
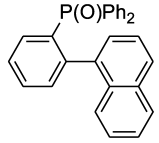
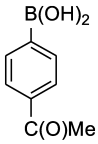
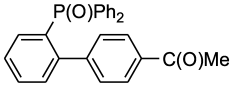
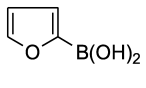
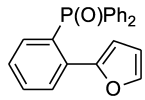
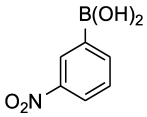
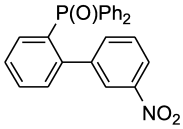
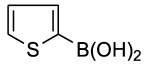
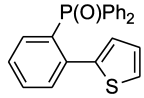
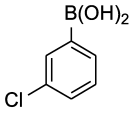
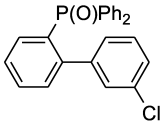
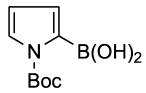
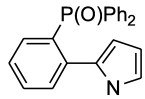
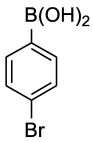
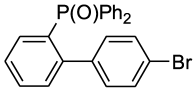
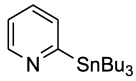
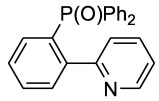
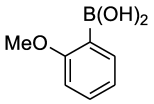
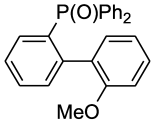
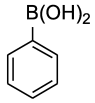
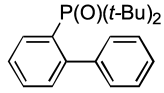
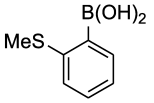
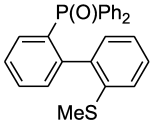
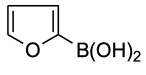
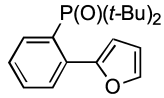
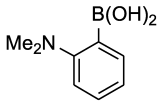
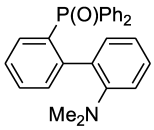
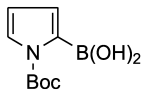
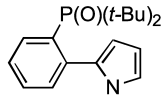
Our synthesis starts with the preparation of the bromophosphine oxide **1**. To enhance the catalytic nature of the overall methodology, the P–C coupling procedures developed by Stelzer were used, in which palladium is used to couple diphenylphosphine or diphenylphosphine oxide with various aryl halides.[13] Compound **1** could be obtained in 92% yield by coupling diphenylphosphine with 1,2-bromoiodobenzene with 1.1 equiv. of NaOAc in the presence of $Pd(OAc)_2$ in DMAc at 130 °C, followed by oxidation with H_2O_2. The starting block **1** was also obtained in 65% yield by the direct coupling of diphenylphosphine oxide with 1,2-bromoiodobenzene. The catalyst used was $Pd(dba)_2$, this time in the presence of 1,3-bis(diphenylphosphino)propane (DPPP) and using $(i\text{-Pr})_2NEt$ as base in toluene at 120 °C. This direct coupling results in a lower yield and requires longer reaction times; but the oxidation step is no longer necessary. The phosphine oxide starting material is a stable solid compared to the air- and moisture-sensitive free phosphine.

The coupling partners to **1** are the boronic acids **2a**–**n** (Table 1). All of these are commercially available, apart from 2-*N*,*N*-dimethylaminophenylboronic acid **2i**,[14] and 1-*t*-butoxycarbonylpyrrol-2-yl boronic acid **2n**,[15] which were synthesised according to literature procedures. Thus, dimethylaniline and pyrrole were *ortho*-lithiated, quenched with $B(OMe)_3$ and acidified, leading to **2i** and **2n** in ca. 50% isolated yield, respectively. In the case of pyrrole, *N*-Boc-protection was necessary first; but the Boc group would be removed after the Suzuki coupling step (vide infra). We were unsuccessful in synthesising 2-pyridinylboronic acid,[16a] required for the synthesis of **3o**. However, the corresponding stannane, 2-pyridinyltributyltin **2o**,[16b] could readily be accessed, which could yield **3o** via the Stille reaction.

The key to our methodology is the Suzuki cross coupling step. Generally, the coupling reaction was conducted using equimolar amounts of **1** and arylboronic acids **2** and 2 equiv. of a base (K_3PO_4) in dioxane at 105 °C. The palladium catalyst was formed in situ from $Pd(dba)_2$ and 4 equiv. of PPh_3. Table 1 illustrates the compounds obtained and their corresponding yields. The *ortho*-positioned $OPPh_2$ moiety in **1** represents a considerably more bulky substituent than those typically encountered in other Suzuki reactions. Consequently, it might be expected that a ligand such as PPh_3, chosen for its ease of handling and availability, would be inferior in comparison to PR_3 (R=Cy, *t*-Bu) or those based on biphenyls, which are considerably more electron-rich and bulky and have been shown to be highly effective towards Suzuki coupling involving considerable steric hindrance.[6] However, **1** couples readily under the aforementioned conditions with phenylboronic acid **2a** as well as *meta*- and *para*-substituted arylboronic acids **2b**–**d** to give the corresponding biaryls in good yields. The reactions preceded equally well with electron-rich and -deficient boronic acids, and they illustrated the expected tolerance of the Suzuki coupling step to various functionalities, including ether, nitro and carbonyl groups. However, some difficulty was experienced with the coupling of **1** with the halo-substituted arylboronic acids **2e** and **2f**, using the conditions described, in which the coupling partners were directly mixed; lower yields of **3e** and **3f** resulted, probably due to arylboronic acid homo-coupling. To obtain reasonable yields, slow introduction of the boronic acids via a dropping funnel during the course of the reaction was necessary; thereby good yields of coupling products were delivered. The presence of halogen functional groups makes phosphines derived from these oxides open to the possibility of accessing polymer or solid-bound biphenyl-based phosphines, analogues of which have been employed for the Suzuki coupling of aryl bromides and chlorides.[17]

As with other Suzuki reactions, the coupling of **1** was significantly more difficult with arylboronic acids containing *ortho*-substituents (**2g**–**j**) to give di-*ortho*-substituted

Table 1. Suzuki coupling of **2** with **1** and **5** leading to **3** and **6**

Boronic acid		Products **3a–i**	Yield (%)[a]	Boronic acid		Products **3j–6n**	Yield (%)
	**2a**		83		**2j**		74[b]
	**2b**		72		**2k**		71[b]
	**2c**		78		**2l**		90[b]
	**2d**		76		**2m**		81[b]
	**2e**		72		**2n**		83[b,c]
	**2f**		66		**2o**		51[b,d]
	**2g**		95[b]		**2a**		81[e]
	**2h**		75[b]		**2l**		84[e]
	**2i**		66[b]		**2n**		75[b,c,f]

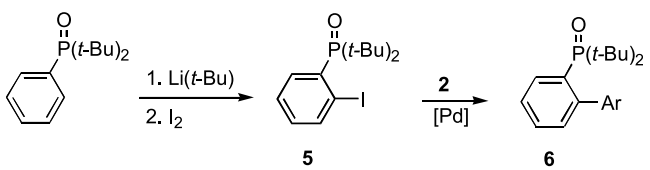
[a] Conditions: 1.0 equiv. **2**, 2.0 equiv. K_3PO_4, 3 mol% $Pd(dba)_2$, 12 mol% PPh_3, dioxane, 105 °C, 12 h.
[b] 2.0 equiv. **2**, reaction run for 48 h.
[c] 3.0 equiv. Na_2CO_3 used as base, DMF, 130 °C.
[d] 5 mol% $Pd(dba)_2$, 20 mol% PPh_3, 1.0 equiv. CuO, DMF, 100 °C.
[e] 1.5 equiv. **2**, 3.3 equiv. KF, 5 mol% $Pd(dba)_2$, 20 mol% PCy_3, dioxane, 105 °C, 24 h.
[f] 5 mol% $Pd(dba)_2$, 20 mol% PPh_3, DMF.

biaryls. Under the conditions outlined above, the reaction proceeded sluggishly, with very low yields of biaryls (**3g–j**) produced. With extra addition of boronic acid and a prolonged reaction time, however, good to excellent yields of products were obtained using the Pd/PPh_3 catalyst. P(*t*-Bu)$_3$ was also examined for the reaction of **1** with 2-methoxyphenylboronic acid **2g**, and 2-methylthiophenylboronic acid **2h**, as it had been reported to outperform PPh_3 in the cross-coupling of aryl chlorides and arylboronic acids, and to be tolerant of *ortho*-substitution in both substrates.[7a] However, the reported conditions, when applied to our reactions, gave lower yields (71% for **2g** and 54% for **2h**) than those obtained with PPh_3. This may be due to the fact that P(*t*-Bu)$_3$ is sterically too demanding for the phosphinyl group. Fu has observed that the sterically less hindered PCy_3 is more effective than P(*t*-Bu)$_3$ in the Suzuki coupling of aryl chlorides that lead to tri-*ortho*-substituted biaryls.[7a] It may also be partly due to

experimental factors. P(*t*-Bu)$_3$ is a viscous oil at room temperature, and transferring accurate catalytic amounts from storage vial to reaction vessel is problematic. As previously discussed, the metal/ligand ratio can have dramatic influence on such C–C coupling reactions;[7a] thus it is vital that the amount of ligand added to a reaction can be carefully controlled. In this context, the phosphonium salts derived from P(*t*-Bu)$_3$ and developed by Fu could be a good alternative.[18] In contrast, the naphthylboronic acid **2k** coupled readily with **1** under the standard conditions to give **3k** in good yield. However, a more bulky variant, 2-(1-methoxynaphthalene)boronic acid, failed to couple with **1** under various conditions, including replacing PPh_3 with P(*t*-Bu)$_3$ and using different bases. Use of DMF as solvent at higher temperatures also proved unsuccessful. A successful coupling of such sterically hindered substrates may demand the use of a new catalyst.[5c]

The last sub-category of biaryls synthesised according to Scheme 2 differs in that they incorporate the heterocycles furan, thiophene, pyrrole and pyridine. Few examples exist in the literature for the synthesis of heterocyclic biaryl compounds via the Suzuki or Stille reaction.[19] Using the same conditions used for **2a**–**d**, compound **1** readily underwent coupling with the heterocyclic boronic acids **2l** and **2m** to yield the expected phosphine oxides **3l** and **3m** in good yields, though these conditions were unsuccessful when **2n** was applied, in which case only starting material was recovered. However, the coupling of **2n** proceeded smoothly when a modified procedure for pyrrole and indole 2-boronic acids was adopted.[20] Thus, under Pd(0)–PPh_3 catalysis in aqueous DMF in the presence of Na_2CO_3 at 130 °C, the reaction went to completion, furnishing **3n** in 83% yield. Contrary to the literature example,[20] there is no need to remove the *N*-Boc-protecting group after the reaction, as it is displaced either during the reaction or in workup. To synthesise **3o**, a different strategy to the Suzuki reaction was applied, due to the unavailability of the necessary boronic acid. The corresponding stannane **2o** was utilised instead, and **3o** was accessed via the Stille reaction. The reaction was run at 100 °C for 24 h in DMF in the presence of Pd(dba)$_2$ and PPh_3. A higher yield of 51% was obtained when 1 equiv. of CuO was added compared to 35% without an additive. Previously, it has been reported that the Stille reaction of **2o** proceeds faster and with higher yields when cupric oxide is used as additive.[21]

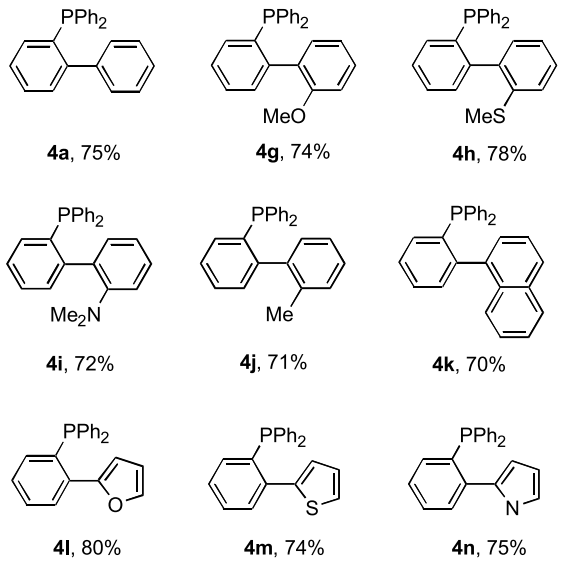
The methodology is also applicable to the synthesis of analogous dialkylphosphines. Scheme 3 shows the synthesis of biaryls containing a di-*t*-butylphosphinyl unit. The *ortho*-iodinated OP(*t*-Bu)$_2$(*o*-C_6H_4I) **5** coupled with **2a**, **2l** or **2n**, furnishing **6a**, **6l** and **6n** in good yields (Table 1). The coupling of **5** with **2a** and **2l** required the more bulky PCy_3 as ligand for palladium, probably due to the much increased steric hindrance of the transmetallation step. With PCy_3,



Scheme 3.

active Pd(0)–monophosphine species could be generated, which should be more easily accessible to the substrates than a Pd(0)L$_2$ species. Since a number of such dialkylphosphines have already been reported,[5h] only three examples are provided in Table 1. The starting iodophosphine oxide **5** can be easily accessed via the method developed by Snieckus.[22]

The free phosphines **4** can be easily obtained from the oxides **3** by reduction with trichlorosilane (Scheme 2). This standard method of phosphine reduction was carried out by simply heating a mixture of **3**, trichlorosilane and triethylamine in toluene at 120 °C overnight. Selected examples of reduction are seen in Scheme 4. In general, the phosphines **4** were obtained as white crystallised solids in good yields. The exception to this was **4l**, which was off-white in colour, and **4n**, which gradually turned pale orange. Compound **4m** could not readily be obtained as a solid. The crystallised form was obtained by cooling in a dry ice/acetone bath; but when allowed to warm to room temperature, an oil was formed.



Scheme 4.

3. Conclusions

We have previously shown that the Heck and related reactions can provide a powerful route to arylphosphines with special solubility properties.[12] The work presented here highlights a general programme based on the Suzuki and, to a limited degree, Stille coupling reactions, for the simple preparation of various biphenyl and hetero-biaryl phosphine ligands, P^X (X=C, N, O, S), in which their stereoelectronic properties can be varied in a systematic fashion, thus enabling rapid catalyst screening and mechanistic study. The elegant work of Buchwald demonstrates further the utility of the method by showing the feasibility of introducing axial chirality.[11b] The hemilabile P^X ligands are worthy of special note. Hemilabile ligands have been extensively studied in coordination chemistry, homogeneous catalysis and materials chemistry, and many examples of their successful applications in these areas exist in the literature.[10] However, few biphenyl and

hetero-biaryl hemilabile phosphines have been reported. The Suzuki coupling protocol now makes these ligands readily accessible, thus opening the door for their chemistry to be investigated.

4. Experimental

4.1. General considerations

All reactions were carried out under an argon atmosphere. Dioxane and THF were distilled under N_2 over sodium benzophenone ketyl, toluene, DMF and triethylamine distilled over CaH. Diphenylphosphine and arylboronic acids were purchased from Aldrich, unless otherwise stated. 2-*N*,*N*-Dimethylaminophenylboronic acid **2i**,[14] 1-*t*-butoxycarbonylpyrrol-2-yl boronic acid **2n**,[15] and 2-pyridinyltributyltin **2o**[16b] were prepared according to published procedures. Elemental analysis was performed by the Microanalysis Laboratory, Department of Chemistry, University of Liverpool.

4.1.1. 2-Diphenylphosphinylbromobenzene (1). *Method A*. An oven-dried, 100 mL Schlenk tube equipped with a magnetic stir bar, a rubber septum and a reflux condenser was charged with NaOAc (2.59 g, 31.6 mmol), $Pd(OAc)_2$ (35 mg, 0.14 mmol) and *N*,*N*-dimethylacetamide (65 mL). 1,2-Bromoiodobenzene **3** (3.7 mL, 29 mmol) and diphenylphosphine (5.0 mL, 29 mmol) were added via syringe and heated at 130 °C for 3 days. The reaction was cooled to room temperature, and the mixture diluted with water (50 mL) and extracted with $CHCl_3$. The combined organic extracts were concentrated in vacuo, and purified by flash chromatography (1:2 EtOAc/hexane) to yield 2-diphenylphosphinobromobenzene[13] as a white precipitate (9.00 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.57 (m, 1H), 7.38–7.32 (m, 6H), 7.30–7.25 (m, 4H), 7.21–7.16 (m, 2H), 6.77–6.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3 (d, J_{CP}=11.2 Hz), 136.2 (d, J_{CP}=10.4 Hz), 134.9, 134.4 (d, J_{CP}=20.0 Hz), 133.4 (d, J_{CP}=2.4 Hz), 130.6, 130.5 (d, J_{CP}=30.2), 129.4, 129.1 (d, J_{CP}=7.2 Hz), 127.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ −3.9. Anal. Calcd for $C_{18}H_{14}PBr$: C, 63.34; H, 4.10. Found: C, 63.16; H, 4.07.

To a solution of 2-diphenylphosphinobromobenzene (9.00 g, 26.4 mmol) in 50 mL MeOH, a couple of drops of 30% H_2O_2 were added at 0 °C and stirred for 1 h at room temperature. The product was partitioned between 100 mL $CHCl_3$ and 50 mL H_2O. The phases were separated and the organic layer was washed with brine (50 mL), dried over $MgSO_4$ and evaporated in vacuo to give **1** as a white precipitate, quantitatively. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.65 (m, 5H), 7.58–7.31 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3 (d, J_{CP}=10.4 Hz), 135.2 (d, J_{CP}=8.0 Hz), 133.7 (d, J_{CP}=2.4 Hz), 133.5 (d, J_{CP}=104.7 Hz), 132.5 (d, J_{CP}=9.6 Hz), 132.3 (d, J_{CP}=2.4 Hz), 132.2 (d, J_{CP}=107.9 Hz), 128.9 (d, J_{CP}=12.0 Hz), 127.3 (d, J_{CP}=11.2 Hz), 127.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2. Anal. Calcd for $C_{18}H_{14}POBr$: C, 60.59; H, 3.93. Found: C, 60.54; H, 3.96.

Method B. An oven-dried, 100 mL Schlenk tube equipped with a magnetic stir bar, a rubber septum and a reflux condenser was charged with diphenylphosphine oxide (6.86 g, 34.0 mmol), $Pd(dba)_2$ (0.56 g, 1.2 mmol) and DPPP (0.42 g, 1.2 mmol) in 50 mL toluene. 1,2-Bromoiodobenzene (5.2 mL, 41 mmol), and (*i*-Pr)$_2$NEt (7.4 mL, 43 mmol) was added via syringe and the mixture refluxed at 120 °C for 4 days. After cooling to room temperature, the product was partitioned between 100 mL $CHCl_3$ and 50 mL H_2O. The phases were separated and the organic layer was washed with brine (50 mL), dried over $MgSO_4$ and evaporated in vacuo to give a pale orange precipitate. Purification by flash chromatography (2:1 EtOAc/hexane) gave the title compound **1** as a white solid (7.90 g, 65% yield).

4.2. General procedure for the Suzuki coupling of 1 with arylboronic acids 2

To a Schlenk tube were charged $OPPh_2$(*o*-C_6H_4Br) **1** (0.50 g, 1.4 mmol) and arylboronic acid (1.4 mmol) together with $Pd(dba)_2$ (24 mg, 0.04 mmol), PPh_3 (44 mg, 0.17 mmol) and K_3PO_4 (0.59 g, 2.8 mmol) in 5 mL of dioxane under an atmosphere of argon. The Schlenk tube was stirred at 105 °C for 12 h and cooled to room temperature. The mixture was diluted with water (10 mL) and extracted with $CHCl_3$ (3×20 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by flash chromatography (2:1 EtOAc/hexane).

4.2.1. 2-Diphenylphosphinylbiphenyl (3a). The reaction was conducted according to the general procedure. Crystallisation from EtOAc/hexane yielded 0.42 g (83%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.52 (m, 5H), 7.45–7.18 (m, 11H), 7.08–7.01 (M, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7 (d, J_{CP}=4.0 Hz), 134.4 (d, J_{CP}=12.0 Hz), 133.5 (d, J_{CP}=103.8 Hz), 132.4, 132.3, 132.0 (d, J_{CP}=8.8 Hz), 132.0, 131.6, 131.5 (d, J_{CP}=3.2 Hz), 130.5, 128.4, 128.0 (d, J_{CP}=97.5 Hz), 127.5, 126.9 (d, J_{CP}=12.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9. Anal. Calcd for $C_{24}H_{19}PO$: C, 81.33; H, 5.41. Found: C, 81.23; H, 5.39. This compound was previously obtained via a multi-lithiation procedure from $OPPh_3$.[23]

4.2.2. 2-Diphenylphosphinyl-4′-methoxybiphenyl (3b). The reaction was conducted according to the general procedure. Crystallisation from EtOAc/hexane yielded 0.39 g (72%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.27 (m, 14H), 7.14 (d, 2H, J=8.7 Hz), 6.57 (d, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9 (d, J_{CP}=8.0 Hz), 134.4 (d, J_{CP}=12.0 Hz), 133.7 (d, J_{CP}=103.9 Hz), 133.3 (d, J_{CP}=4.0 Hz), 133.1 (d, J_{CP}=115.8 Hz), 132.4 (d, J_{CP}=9.6 Hz), 132.1 (d, J_{CP}=2.4 Hz), 131.9, 131.9 (d, J_{CP}=9.6 Hz), 131.4 (d, J_{CP}=3.2 Hz), 128.9 (d, J_{CP}=12.8 Hz), 128.4 (d, J_{CP}=12.0 Hz), 126.7 (d, J_{CP}=12.0 Hz), 113.1, 55.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9. Anal. Calcd for $C_{25}H_{21}PO_2$: C, 78.10; H, 5.52. Found: C, 77.80; H, 5.51.

4.2.3. 2-Diphenylphosphinyl-4′-acetylbiphenyl (3c). The reaction was conducted according to the general procedure. Crystallisation from EtOAc/hexane yielded 0.43 g (78%) of the title compound as white crystals. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.64 (d, 2H, J=8.3 Hz), 7.59–7.29 (m, 14H), 7.31 (d, 2H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 146.9, 145.6, 136.1, 134.4 (d, J_{CP}=12.0 Hz), 133.3 (d, J_{CP}=104.7 Hz), 132.2 (d, J_{CP}=2.4 Hz), 132.1, 131.9 (d, J_{CP}=9.6 Hz), 131.7 (d, J_{CP}=2.4 Hz), 131.4 (d, J_{CP}=115.0 Hz), 128.9 (d, J_{CP}=12.0 Hz), 128.6 (d, J_{CP}=12.8 Hz), 127.5, 127.5 (d, J_{CP}=12.8 Hz), 26.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9. Anal. Calcd for $C_{26}H_{21}PO_2$: C, 78.78; H, 5.34. Found: C, 78.39; H, 5.43.

4.2.4. 2-Diphenylphosphinyl-3′-nitrobiphenyl (3d). The reaction was conducted according to the general procedure. Crystallisation from EtOAc/hexane yielded 0.42 g (76%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.26 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 135.8 (d, J_{CP}=107.9 Hz), 135.7 (d, J_{CP}=105.5 Hz), 134.2 (d, J_{CP}=12.0 Hz), 133.8 (d, J_{CP}=2.4 Hz), 132.5 (d, J_{CP}=10.4 Hz), 132.4 (d, J_{CP}=3.2 Hz), 131.9 (d, J_{CP}=9.6 Hz), 128.9 (d, J_{CP}=12.0 Hz), 128.9, 128.8 (d, J_{CP}=12.0 Hz), 128.4, 127.9 (d, J_{CP}=12.0 Hz), 127.3 (d, J_{CP}=11.2 Hz), 125.1, 122.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.6. Anal. Calcd for $C_{24}H_{18}PO_3N$: C, 72.17; H, 4.55; N, 3.50. Found: C, 71.94; H, 4.59; N, 3.28.

4.2.5. 2-Diphenylphosphinyl-3′-chlorobiphenyl (3e). The reaction was conducted according to the general procedure, with the exception that the arylboronic acid **2e** was added slowly (over 6 h) during the course of the reaction via a dropping funnel in 5 mL dioxane. Crystallisation from EtOAc/hexane yielded 0.39 g (72%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.53 (m, 4H), 7.44–7.26 (m, 10H), 7.15–7.10 (m, 2H), 7.02–6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8 (d, J_{CP}=8.8 Hz), 139.1 (d, J_{CP}=4.0 Hz), 134.3 (d, J_{CP}=12.0 Hz), 133.7, 133.3 (d, J_{CP}=104.7 Hz), 133.1, 132.1 (d, J_{CP}=9.6 Hz), 132.1 (d, J_{CP}=2.4 Hz), 132.0 (d, J_{CP}=9.6 Hz), 131.9, 131.7 (d, J_{CP}=2.4 Hz), 131.5, 131.0, 128.5, 128.1 (d, J_{CP}=98.3 Hz), 127.2 (d, J_{CP}=12.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9. Anal. Calcd for $C_{24}H_{18}POCl$: C, 74.12; H, 4.68. Found: C, 74.19; H, 4.69.

4.2.6. 2-Diphenylphosphinyl-4′-bromobiphenyl (3f). The reaction was conducted according to the general procedure, with the exception that the arylboronic acid **2f** was added slowly (over 6 h) during the course of the reaction via a dropping funnel in 5 mL dioxane. Crystallisation from EtOAc/hexane yielded 0.40 g (66%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.52 (m, 5H), 7.44–7.25 (m, 9H), 7.17–7.14 (d, 2H, J=8.6 Hz), 7.07–7.04 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8 (d, J_{CP}=8.8 Hz), 139.5 (d, J_{CP}=4.0 Hz), 134.3 (d, J_{CP}=12.0 Hz), 133.3 (d, J_{CP}=104.7 Hz), 132.0 (d, J_{CP}=104.8 Hz), 132.2, 132.2 (d, J_{CP}=2.4 Hz), 132.0 (d, J_{CP}=9.6 Hz), 132.0 (d, J_{CP}=9.6 Hz), 131.7 (d, J_{CP}=3.2 Hz), 130.6, 128.5 (d, J_{CP}=12.0 Hz), 127.3 (d, J_{CP}=12.0 Hz), 122.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9. Anal. Calcd for $C_{24}H_{18}POBr$: C, 66.59; H, 4.16. Found: C, 66.57; H, 4.17.

4.2.7. 2-Diphenylphosphinyl-2′-methoxybiphenyl (3g). The reaction was conducted according to the general procedure; with the exception that the reaction time was increased to 48 h, and an extra equivalent (1.40 mmol) of the arylboronic acid **2g** was added after 24 h. Crystallisation from EtOAc/hexane yielded 0.51 g (95%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.15 (m, 15H), 7.05 (ddd, 1H, J=8.0, 8.0, 1.8 Hz), 6.80 (ddd, 1H, J=7.3, 7.3, 0.8 Hz), 6.35 (d, 1H, J=8.1 Hz), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0 (d, J_{CP}=8.0 Hz), 134.4, 133.7 (d, J_{CP}=111.1 Hz), 133.5 (d, J_{CP}=104.7 Hz), 133.1, 132.5 (d, J_{CP}=8.8 Hz), 131.6 (d, J_{CP}=2.4 Hz), 131.3 (d, J_{CP}=9.6 Hz), 131.0 (d, J_{CP}=2.4 Hz), 129.5, 129.0 (d, J_{CP}=4.0 Hz), 128.5 (d, J_{CP}=12.0 Hz), 127.9 (d, J_{CP}=12.0 Hz), 126.9 (d, J_{CP}=12.0 Hz), 119.7, 109.6, 54.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.2. Anal. Calcd for $C_{25}H_{21}PO_2$: C, 78.10; H, 5.52. Found: C, 77.89; H, 5.66.

4.2.8. 2-Diphenylphosphinyl-2′-methylthiobiphenyl (3h). The reaction was conducted according to the general procedure, with the exception that the reaction time was increased to 48 h, and an extra equivalent (1.40 mmol) of the arylboronic acid **2h** was added after 24 h. Crystallisation from EtOAc/hexane yielded 0.42 g (75%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.67 (m, 2H), 7.60–7.23 (m, 11H), 7.18–7.13 (m, 2H), 7.05–6.94 (m, 2H), 6.66 (dd, 1H, J=7.8, 0.9 Hz), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9 (d, J_{CP}=8.8 Hz), 138.0 (d, J_{CP}=4.0 Hz), 137.9, 135.8 (d, J_{CP}=108.7 Hz), 135.7 (d, J_{CP}=105.5 Hz), 134.6 (d, J_{CP}=12.0 Hz), 132.9 (d, J_{CP}=9.6 Hz), 132.5 (d, J_{CP}=8.8 Hz), 132.5 (d, J_{CP}=9.6 Hz), 132.1, 131.0 (d, J_{CP}=2.4 Hz), 128.9 (d, J_{CP}=12.0 Hz), 128.6, 128.5 (d, J_{CP}=12.0 Hz), 124.0, 123.7, 15.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. Anal. Calcd for $C_{25}H_{21}POS$: C, 74.97; H, 5.30. Found: C, 74.68; H, 5.25.

4.2.9. 2-Diphenylphosphinyl-2′-dimethylaminobiphenyl (3i). The reaction was conducted according to the general procedure with the exception that the reaction time was increased to 48 h, and an extra equivalent (1.40 mmol) of the arylboronic acid **2i** was added after 24 h. Crystallisation from EtOAc/hexane yielded 0.36 g (66%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.30 (m, 13H), 7.15–7.10 (m, 1H), 6.85–6.67 (m, 4H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0 (d, J_{CP}=12.0 Hz), 134.9 (d, J_{CP}=103.9 Hz), 133.1 (d, J_{CP}=10.4 Hz), 132.3 (d, J_{CP}=9.6 Hz), 132.1 (d, J_{CP}=10.4 Hz), 132.0, 131.8, 131.4, 130.6 (d, J_{CP}=101.5 Hz), 129.0, 128.9, 128.4 (d, J_{CP}=12.0 Hz), 128.3 (d, J_{CP}=12.0 Hz), 126.4 (d, J_{CP}=12.0 Hz), 120.9, 117.9, 43.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.4. Anal. Calcd for $C_{26}H_{24}PON$: C, 78.56; H, 6.10; N, 3.52. Found: C, 78.29; H, 6.05; N, 3.38.

4.2.10. 2-Diphenylphosphinyl-2′-methylbiphenyl (3j). The reaction was conducted according to the general procedure with the exception that the reaction time was increased to 48 h, and an extra equivalent (1.40 mmol) of the arylboronic acid **2j** was added after 24 h. Crystallisation from EtOAc/hexane yielded 0.38 g (74%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–6.92 (m, 18H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 134.2 (d, J_{CP}=12.0 Hz), 133.5 (d, J_{CP}=103.9 Hz), 133.3 (d, J_{CP}=103.9 Hz), 132.3 (d, J_{CP}=9.6 Hz), 131.9 (d, J_{CP}=3.2 Hz), 131.8 (d, J_{CP}=9.6 Hz), 131.5 (d, J_{CP}=3.2 Hz), 131.5 (d, J_{CP}=2.4 Hz), 131.1, 129.7, 128.4 (d, J_{CP}=12.0 Hz), 128.3 (d, J_{CP}=12.0 Hz), 127.9, 127.0 (d,

J_{CP}=12.8 Hz), 124.6, 20.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.7. Anal. Calcd for $C_{25}H_{21}PO$: C, 81.50; H, 5.76. Found: C, 81.33; H, 5.72.

4.2.11. 1-(2-Diphenylphosphinylphenyl)naphthalene (3k). The reaction was conducted according to the general procedure. Crystallisation from EtOAc/hexane yielded 0.40 g (71%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.67 (m, 1H), 7.63–7.17 (m, 17H), 6.97–6.92 (m, 1H), 6.87–6.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.7 (d, J_{CP}=11.2 Hz), 133.4 (d, J_{CP}=11.2 Hz), 133.2, 132.3 (d, J_{CP}=8.8 Hz), 132.0, 131.6, 131.5 (d, J_{CP}=12.0 Hz), 131.5, 131.0 (d, J_{CP}=9.6 Hz), 130.5 (d, J_{CP}=3.2 Hz), 129.8, 128.6, 128.4, 128.3, 128.2, 127.7, 127.5 (d, J_{CP}=12.0 Hz), 127.0 (d, J_{CP}=108.6 Hz), 125.6, 125.2 (d, J_{CP}=98.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8. Anal. Calcd for $C_{28}H_{21}PO$: C, 83.14; H, 5.24. Found: C, 82.97; H, 5.13.

4.2.12. 2-(2-Diphenylphosphinylphenyl)furan (3l). The reaction was conducted according to the general procedure, with the exception that a longer reaction time of 48 h was employed. Crystallisation from EtOAc/hexane yielded 0.43 g (90%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.72 (m, 14H), 7.16 (d, 1H, J=1.3 Hz), 7.03 (d, 1H, J=3.3 Hz), 6.16 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4 (d, J_{CP}=4.8 Hz), 142.9, 135.0 (d, J_{CP}=7.2 Hz), 135.3 (d, J_{CP}=12.0 Hz), 133.3 (d, J_{CP}=105.5 Hz), 132.4 (d, J_{CP}=2.4 Hz), 132.0 (d, J_{CP}=9.6 Hz), 131.8 (d, J_{CP}=3.2 Hz), 130.1 (d, J_{CP}=9.6 Hz), 130.0 (d, J_{CP}=101.5 Hz), 128.6 (d, J_{CP}=12.0 Hz), 127.6 (d, J_{CP}=12.0 Hz), 112.9, 111.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9. Anal. Calcd for $C_{22}H_{17}PO_2$: C, 76.73; H, 4.99. Found: C, 76.85; H, 4.97.

4.2.13. 2-(2-Diphenylphosphinylphenyl)thiophene (3m). The reaction was conducted according to the general procedure, with the exception that a longer reaction time of 48 h was employed. Crystallisation from EtOAc/hexane yielded 0.41 g (81%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.29 (m, 15H), 7.03 (dd, 1H, J=5.1, 1.1 Hz), 6.74 (dd, 1H, J=5.1, 3.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0 (d, J_{CP}=4.8 Hz), 139.8 (d, J_{CP}=8.0 Hz), 134.7 (d, J_{CP}=12.0 Hz), 132.8 (d, J_{CP}=105.5 Hz), 132.8 (d, J_{CP}=8.8 Hz), 132.8, 131.8, 131.6 (d, J_{CP}=9.6 Hz), 131.2 (d, J_{CP}=2.4 Hz), 131.2 (d, J_{CP}=114.2 Hz), 128.2 (d, J_{CP}=12.8 Hz), 127.1 (d, J_{CP}=12.0 Hz), 127.0, 126.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.9. Anal. Calcd for $C_{22}H_{17}POS$: C, 73.31; H, 4.77. Found: C, 73.43; H, 4.76.

4.2.14. 2-(2-Diphenylphosphinylphenyl)pyrrole (3n). The reaction was conducted according to the general procedure; with the exception that 3 equiv. of Na_2CO_3 was used as base, and the reaction was heated at 130 °C in DMF for 48 h. Crystallisation from EtOAc/hexane yielded 0.40 g (83%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (br s, 1H), 7.73–7.02 (m, 14H), 6.65 (m, 1H), 6.26 (m, 1H), 5.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3 (d, J_{CP}=8.0 Hz), 134.6 (d, J_{CP}=12.8 Hz), 132.9 (d, J_{CP}=2.4 Hz), 132.9 (d, J_{CP}=93.5 Hz), 132.3 (d, J_{CP}=3.2 Hz), 132.1 (d, J_{CP}=9.6 Hz), 131.6 (d, J_{CP}=4.8 Hz), 131.2, 130.7 (d, J_{CP}=9.6 Hz), 128.8 (d, J_{CP}=12.0 Hz), 127.6 (d, J_{CP}=100.7 Hz), 125.5 (d, J_{CP}=12.8 Hz), 120.1, 109.6 (d, J_{CP}=5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.1. Anal. Calcd for $C_{22}H_{18}PON$: C, 76.95; H, 5.29; N, 4.08. Found: C, 77.00; H, 5.50; N, 3.97.

4.2.15. 2-(2-Diphenylphosphinylphenyl)pyridine (3o). To a Schlenk tube were charged **1** (0.50 g, 1.4 mmol) and 2-pyridyltributyltin **2o** (1.03 g, 2.80 mmol) together with $Pd(dba)_2$ (40 mg, 0.07 mmol), PPh_3 (73 mg, 0.28 mmol) and CuO (0.11 g, 1.4 mmol) in 50 mL of DMF under an atmosphere of argon. The Schlenk tube was stirred at 100 °C for 48 h and cooled to room temperature. The mixture was diluted with water (25 mL) and extracted with $CHCl_3$ (3×50 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and evaporated in vacuo. The crude product was purified by flash chromatography (EtOAc). Crystallisation from EtOAc/hexane yielded 0.25 g (51%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, 1H, J=4.3 Hz), 7.80 (d, 1H, J=7.8 Hz), 7.64–7.56 (m, 6H), 7.48–7.28 (m, 9H), 6.94 (ddd, 1H, J=7.6, 4.8, 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0 (d, J_{CP}=4.0 Hz), 149.1, 146.3 (d, J_{CP}=8.0 Hz), 135.8, 134.7 (d, J_{CP}=12.0 Hz), 133.7 (d, J_{CP}=104.5 Hz), 132.4 (d, J_{CP}=2.4 Hz), 132.0 (d, J_{CP}=8.8 Hz), 131.9 (d, J_{CP}=9.6 Hz), 131.6 (d, J_{CP}=101.5 Hz), 131.5 (d, J_{CP}=3.2 Hz), 128.5 (d, J_{CP}=12.0 Hz), 128.1 (d, J_{CP}=12.0 Hz), 126.1, 122.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3. Anal. Calcd for $C_{23}H_{18}PON$: C, 77.73; H, 5.12; N, 3.94. Found: C, 77.60; H, 5.24; N, 3.77.

4.3. General procedure for the Suzuki coupling of OP(*t*-Bu)$_2$(*o*-C$_6$H$_4$I) 5 with arylboronic acids 2

To a Schlenk tube were charged OP(*t*-Bu)$_2$(*o*-C$_6$H$_4$I) **5** (0.50 g, 1.4 mmol) and arylboronic acid **2** (2.1 mmol), $Pd(dba)_2$ (39 mg, 0.068 mmol), PCy_3 (77 mg, 0.27 mmol) and KF (0.26 g, 4.5 mmol) in 15 mL of dioxane under an atmosphere of argon. The reaction mixture was stirred for 24 h at 105 °C and cooled to room temperature. Dilution with water (25 mL) was followed by extraction with $CHCl_3$ (3×25 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography (5:1 EtOAc/hexane) gave the coupled products **6** (Scheme 3).

4.3.1. 2-Di-*t*-butylphosphinylbiphenyl (6a). The reaction was conducted following the general procedure. Crystallisation from EtOAc/hexane yielded 0.35 g (81%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J=8.9, 8.9 Hz, 1H), 7.46 (dd, J=7.3, 7.3 Hz, 1H), 7.37 (dd, J=7.6, 7.6 Hz, 1H), 7.30–7.20 (m, 6H), 1.25 (d, J=13.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1 (d, J_{CP}=4.0 Hz), 142.7 (d, J_{CP}=2.4 Hz), 133.6 (d, J_{CP}=8.8 Hz), 131.5 (d, J_{CP}=11.2 Hz), 130.3 (d, J_{CP}=2.4 Hz), 129.3, 129.1 (d, J_{CP}=75.9 Hz), 127.0, 126.7, 125.7 (d, J_{CP}=12.0 Hz), 37.4 (d, J_{CP}=58.3 Hz), 27.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.0. Anal. Calcd for $C_{20}H_{27}PO$: C, 76.39; H, 8.67. Found: 76.40; H, 8.73.

4.3.2. 2-(2-Di-*t*-butylphosphinylphenyl)furan (6l). The reaction was conducted following the general procedure. Crystallisation from EtOAc/hexane yielded 0.34 g (84%) of the title compound as white crystals. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.67 (dd, J=8.8, 8.8 Hz, 1H), 7.56 (m, 4H), 6.50–6.41 (m, 2H), 1.28 (d, J=13.4 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4 (d, J_{CP}=3.2 Hz), 141.7, 138.6 (d, J_{CP}=2.4 Hz), 133.6 (d, J_{CP}=8.0 Hz), 131.9 (d, J_{CP}=11.2 Hz), 131.2 (d, J_{CP}=74.3 Hz), 130.6 (d, J_{CP}=2.4 Hz), 126.9 (d, J_{CP}=10.4 Hz), 111.1, 109.1, 37.6 (d, J_{CP}=59.1 Hz), 27.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.0. Anal. Calcd for $C_{18}H_{17}PO_2$: C, 72.96; H, 5.79. Found: 72.81; H, 5.73.

4.3.3. 2-(2-Di-*t*-butylphosphinylphenyl)pyrrole (6n). The reaction was conducted following the general procedure; with the exception that PPh_3 (72 mg, 0.27 mmol) was used instead of PCy_3. The base used was aq. Na_2CO_3 (0.44 g, 4.1 mmol), and the solvent DMF. The reaction was performed at 130 °C, again for 24 h. Crystallisation from EtOAc/hexane yielded 0.31 g (75%) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, J=8.2, 4.3 Hz, 1H), 7.56 (dd, J=12.7, 7.9 Hz, 1H), 7.41 (dd, J=7.7, 7.7 Hz, 1H), 7.11 (dd, J=7.6, 7.6 Hz, 1H), 6.88 (m, 1H), 6.63 (m, 1H), 6.20 (m, 1H) 1.31 (d, J=13.7 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3 (d, J_{CP}=3.2 Hz), 132.8 (d, J_{CP}=12.8 Hz), 131.7 (d, J_{CP}=2.4 Hz), 130.5 (d, J_{CP}=8.8 Hz), 124.0 (d, J_{CP}=75.9 Hz), 123.0 (d, J_{CP}=12.8 Hz), 120.6, 110.3, 109.2, 108.4, 38.4 (d, J_{CP}=58.3 Hz), 28.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 64.0. Anal. Calcd for $C_{18}H_{26}PON$: C, 71.25; H, 8.65; N, 4.62. Found: 71.00; H, 8.55; N, 3.97.

4.4. General procedure for the reduction of oxides 3 to phosphines 4

A 10 mL toluene solution of **3** (1.00 mmol) was frozen in liquid nitrogen, to which trichlorosilane (5 equiv.) and triethylamine (5.5 equiv.) were added. The mixture was stirred at 120 °C under argon overnight. After cooling to room temperature, a saturated $NaHCO_3$ aqueous solution (1 mL) was added, and further stirred for 5 min. This was filtered through a pad of alumina and evaporated in vacuo to give a crude oily product. Purification by flash chromatography (9:1 hexane/EtOAc), and crystallisation in hexane gave the desired product as crystalline solids.

4.4.1. 2-Diphenylphosphinobiphenyl (4a). The general procedure on a 1.2 mmol scale gave 0.30 g (75% yield) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.16 (m, 18H), 7.06 (ddd, 1H, J=7.6, 3.8, 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 148.5, 142.1 (d, J_{CP}=6.4 Hz), 138.1 (d, J_{CP}=12.0 Hz), 136.3 (d, J_{CP}=13.6 Hz), 134.4, 134.3 (d, J_{CP}=20.0 Hz), 130.5 (d, J_{CP}=4.8 Hz), 130.1 (d, J_{CP}=4.0 Hz), 129.0, 128.8, 128.7 (d, J_{CP}=6.4 Hz), 127.9, 127.6 (d, J_{CP}=20.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ −12.0. Anal. Calcd for $C_{24}H_{19}P$: C, 85.20; H, 5.62. Found: C, 84.83; H, 5.65.

4.4.2. 2-Diphenylphosphino-2′-methoxybiphenyl (4g). The general procedure on a 1.3 mmol scale gave 0.36 g (74% yield) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, 1H, J=7.3, 7.3 Hz), 7.32–7.26 (m, 12H), 7.18–7.10 (m, 2H), 7.06 (dd, 1H, J=7.4, 1.6 Hz), 6.90 (dd, 1H, J=7.4, 7.4 Hz), 6.81 (d, 1H, J=8.4 Hz), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 134.6, 134.0 (d, J_{CP}=20.0 Hz), 131.7, 131.7, 130.8 (d, J_{CP}=24.0 Hz), 130.8, 129.4, 129.2 (d, J_{CP}=24.0 Hz), 128.6, 128.6, 128.5, 128.4 (d, J_{CP}=7.2 Hz), 127.7, 120.3, 110.6, 55.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ-11.7. Anal. Calcd for $C_{25}H_{21}PO$: C, 81.50; H, 5.76. Found: C, 81.80; H, 5.95.

4.4.3. 2-Diphenylphosphino-2′-methylthiobiphenyl (4h). The general procedure on a 1.1 mmol scale gave 0.30 g (78% yield) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.39 (m, 1H), 7.34–7.16 (m, 14H), 7.13–7.10 (m, 1H), 6.98–6.94 (m, 1H), 6.81–6.79 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 138.0, 135.2, 134.4, 134.4, 134.2, 133.9 (d, J_{CP}=19.2 Hz), 130.8 (d, J_{CP}=3.2 Hz), 130.5 (d, J_{CP}=5.6 Hz), 129.2, 128.9, 128.7 (d, J_{CP}=7.2 Hz), 128.5 (d, J_{CP}=7.2 Hz), 128.4, 124.8, 124.1, 16.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ −12.3. Anal. Calcd for $C_{25}H_{21}PS$: C, 78.09; H, 5.52. Found: C, 77.89; H, 5.50.

4.4.4. 2-Diphenylphosphino-2′-dimethylaminobiphenyl (4i). The general procedure on a 0.9 mmol scale gave 0.25 g (72% yield) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.37 (m, 2H), 7.33–7.18 (m, 11H), 7.15–7.10 (m, 2H), 7.01–6.91 (m, 3H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1 (d, J_{CP}=12.8 Hz), 136.7 (d, J_{CP}=12.0 Hz), 136.3 (d, J_{CP}=3.2 Hz), 135.6 (d, J_{CP}=6.4 Hz), 133.6 (d, J_{CP}=20.0 Hz), 133.3 (d, J_{CP}=19.2 Hz), 132.2, 130.7 (d, J_{CP}=6.4 Hz), 129.6, 128.9, 128.4 (d, J_{CP}=12.0 Hz), 128.4, 128.1 (d, J_{CP}=16.0 Hz), 127.2, 121.7, 118.0, 43.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ −12.6. Anal. Calcd for $C_{26}H_{24}PN$: C, 81.86; H, 6.35; N, 3.67. Found: C, 81.75; H, 6.36; N, 3.69.

4.4.5. 2-Diphenylphosphino-2′-methylbiphenyl (4j). The general procedure on a 1.0 mmol scale gave 0.26 g (71% yield) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.01 (m, 18H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 137.1 (d, J_{CP}=11.2 Hz), 136.8 (d, J_{CP}=10.2 Hz), 136.7 (d, J_{CP}=11.2 Hz), 135.7, 133.8 (d, J_{CP}=19.3 Hz), 133.7 (d, J_{CP}=20.3 Hz), 130.3 (d, J_{CP}=3.1 Hz), 129.6 (d, J_{CP}=5.1 Hz), 128.6, 128.3 (d, J_{CP}=5.1 Hz), 128.3, 128.2, 127.4, 124.6, 123.2, 20.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ −11.6 Anal. Calcd for $C_{25}H_{21}P$: C, 85.21; H, 6.00. Found: C, 85.33; H, 6.22.

4.4.6. 1-(2-Diphenylphosphinophenyl)naphthalene (4k). The general procedure on a 1.0 mmol scale gave 0.27 g (70% yield) of the title compound as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.79 (m, 2H), 7.46–7.27 (m, 10H), 7.21–7.15 (m, 6H), 7.12–7.05 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.8, 139.5 (d, J_{CP}=6.4 Hz), 138.3 (d, J_{CP}=12.8 Hz), 138.0 (d, J_{CP}=12.0 Hz), 137.8 (d, J_{CP}=12.0 Hz), 134.2 (d, J_{CP}=4.0 Hz), 134.0 (d, J_{CP}=4.8 Hz), 133.7, 132.7, 131.3 (d, J_{CP}=5.6 Hz), 128.9, 128.7 (d, J_{CP}=6.4 Hz), 128.6 (d, J_{CP}=12.0 Hz), 128.6 (d, J_{CP}=20.8 Hz), 128.6, 128.4 (d, J_{CP}=3.2 Hz), 128.2 (d, J_{CP}=8.8 Hz), 126.7, 126.0 (d, J_{CP}=15.2 Hz), 125.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ −13.1. Anal. Calcd for $C_{28}H_{21}P$: C, 86.57; H, 5.46. Found: C, 86.10; H, 5.62.

4.4.7. 2-(2-Diphenylphosphinophenyl)furan (4l). The general procedure on a 1.2 mmol scale gave 0.32 g (80% yield) of the title compound as white crystals. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.76–7.72 (m, 1H), 7.41–7.16 (m, 13H), 6.96 (dd, 1H, J=7.7, 4.2 Hz), 6.50–6.49 (m, 1H), 6.37–6.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 142.5, 137.7 (d, J_{CP}=11.2 Hz), 136.6 (d, J_{CP}=26.4 Hz), 134.9, 134.8, 134.3 (d, J_{CP}=20.0 Hz), 129.1, 129.0, 128.9, 128.6 (d, J_{CP}=4.8 Hz), 127.9, 111.7, 111.0 (d, J_{CP}= 12.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ −8.3. Anal. Calcd for $C_{22}H_{17}PO$: C, 80.47; H, 5.23. Found: C, 80.11; H, 5.2.

4.4.8. 2-(2-Diphenylphosphinophenyl)thiophene (4m). The general procedure on a 1.1 mmol scale gave 0.29 g (74% yield) of the title compound as an off-white oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50–7.47 (m, 1H), 7.32–7.22 (m, 13H), 7.01 (dd, 1H, J=7.8, 3.7 Hz), 6.93 (m, 1H), 6.85 (dd, 1H, J=3.5, 1.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9 (d, J_{CP}=6.4 Hz), 140.7 (d, J_{CP}=28.8 Hz), 138.1 (d, J_{CP}=12.0 Hz), 137.4 (d, J_{CP}=15.2 Hz), 134.7, 134.3 (d, J_{CP}=20.0 Hz), 131.6 (d, J_{CP}=4.8 Hz), 128.9 (d, J_{CP}= 5.6 Hz), 128.9, 128.9, 128.5 (d, J_{CP}=5.6 Hz), 128.3, 127.1, 126.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ −11.5.

4.4.9. 2-(2-Diphenylphosphinophenyl)pyrrole (4n). The general procedure on a 1.2 mmol scale gave 0.29 g (75% yield) of the title compound as white crystals. ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (br s, 1H) 7.58–7.25 (m, 12H), 7.14 (ddd, 1H, J=7.5, 7.5, 1.3 Hz), 6.96 (ddd, 1H, J=7.8, 4.4, 1.3 Hz), 6.73 (m, 1H), 6.24 (m, 1H), 6.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5 (d, J_{CP}=10.4 Hz), 134.9, 134.3 (d, J_{CP}=20.0 Hz), 132.1 (d, J_{CP}=9.6 Hz), 130.7 (d, J_{CP}=10.4 Hz), 129.7 (d, J_{CP}=5.6 Hz), 129.4, 129.2, 129.0 (d, J_{CP}=7.2 Hz), 128.8 (d, J_{CP}=9.6 Hz), 127.2, 118.8, 110.3 (d, J_{CP}=4.0 Hz), 109.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ −10.0. Anal. Calcd for $C_{22}H_{18}PN$: C, 80.71; H, 5.55; N, 4.28. Found: C, 80.48; H, 5.58; N, 4.23.

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References and notes

1. (a) In *Applied homogeneous catalysis with organometallic reagents*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weinheim, Germany, 1996. (b) In *Catalytic asymmetric synthesis*; Ojima, I., Ed.; Wiley-VCH: New York, 2000.
2. For examples, see: (a) Mikami, K.; Korenaga, T.; Terada, M.; Ohkuma, T.; Pham, T.; Noyori, R. *Angew. Chem. Int. Ed.* **1999**, *38*, 495. (b) Ogasawara, M.; Yoshida, K.; Hayashi, T. *Organometallics* **2000**, *19*, 1567. (c) Ogasawara, M.; Ikeda, H.; Ohtsuki, H.; Hayashi, T. *Chem. Lett.* **2000**, *7*, 776. (d) Mikami, K.; Aikawa, K.; Korenaga, T. *Org. Lett.* **2001**, *3*, 243. (e) Tang, W.; Chi, Y.; Zhang, X. *Org. Lett.* **2002**, *4*, 1695. (f) Henschke, J. P.; Zanotti-Gerosa, A.; Moran, P.; Harrison, P.; Mullen, B.; Casey, G.; Lennon, I. C. *Tetrahedron Lett.* **2003**, *44*, 4379. (g) Ratovelomanana-Vidal, V.; Girard, C.; Touati, R.; Tranchier, J. P.; Ben Hassine, B.; Genet, J. P. *Adv. Synth. Catal.* **2003**, *345*, 261. and references cited therein.
3. Kadyrov, R.; Heinicke, J.; Kindermann, M. K.; Heller, D.; Fischer, C.; Selke, R.; Fischer, A. K.; Jones, P. G. *Chem. Ber.* **1997**, *130*, 1663.
4. Tsuruta, H.; Imamoto, T. *Synlett* **2001**, 999.
5. For examples of biphenyl-based ligands in C–C coupling reactions, see: (a) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **1999**, *38*, 2413. (b) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550. (c) Yin, J.; Rainka, M. P.; Zhang, X.-X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162. For C–N coupling reactions, see: (d) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722. (e) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J. J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158. For C–O coupling reactions, see: (f) Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1997**, *119*, 11108. (g) Ahman, J.; Wolfe, J. P.; Troutman, M. V.; Palucki, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722. See also for preparation methods and applications of biphenyl and related phosphines: (h) Buchwald, S. L.; Old, D. W.; Wolfe, J. P.; Palucki, M.; Kamikawa, K. US 6,307,087, 2001.
6. Littke, A. F.; Fu, G. C. *Angew. Chem. Int. Ed.* **2002**, *41*, 4176.
7. (a) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020. (b) Hu, Q.-S.; Lu, Y.; Tang, Z. Y.; Yu, H.-B. *J. Am. Chem. Soc.* **2003**, *125*, 2856. (c) Niyomura, O.; Tokunaga, M.; Obora, Y.; Iwasawa, T.; Tsuji, Y. *Angew. Chem. Int. Ed.* **2003**, *42*, 1287. (d) Reid, S. M.; Boyle, R. C.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 7816.
8. (a) Tomori, H.; Fox, J. M.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 5334. (b) Kaye, S.; Fox, J. M.; Hicks, F. A.; Buchwald, S. L. *Adv. Synth. Catal.* **2001**, *343*, 789.
9. Baillie, C.; Chen, W.; Xiao, J. *Tetrahedron Lett.* **2001**, *42*, 9085.
10. For examples, see: (a) Slone, C. S.; Weinberger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *48*, 233. (b) Espinet, P.; Soulantica, K. *Coord. Chem. Rev.* **1999**, *193–195*, 499. (c) Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1975. (d) Kuriyama, M.; Nagai, K.; Yamada, K.; Miwa, Y.; Taga, T.; Tomioka, K. *J. Am. Chem. Soc.* **2002**, *124*, 8932. (e) Steyer, S.; Jeunesse, C.; Matt, D.; Welter, R.; Wesolek, M. *J. Chem. Soc., Dalton Trans.* **2002**, 4264. (f) Eisenberg, A. H.; Ovchinnikov, M. V.; Mirkin, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 2836.
11. (a) Trost, B. M.; Marschner, C. *Bull. Soc. Chim. Fr.* **1997**, *134*, 263. (b) Yin, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 12051. (c) Yu, H.; Hu, Q.; Pu, L. *J. Am. Chem. Soc.* **2000**, *122*, 6500. (d) Tang, W.; Chi, Y.; Zhang, X. *Org. Lett.* **2002**, *4*, 1695.
12. (a) Chen, W.; Xu, L.; Xiao, J. *Org. Lett.* **2000**, *2*, 2675. (b) Chen, W.; Xiao, J. *Tetrahedron Lett.* **2000**, *41*, 3697. (c) Hu, Y.; Chen, W.; Xu, L.; Xiao, J. *Organometallics* **2001**, *14*, 3206. (d) Chen, W.; Xu, L.; Hu, Y.; Banet, A. M.; Xiao, J. *Tetrahedron* **2002**, *58*, 3889. (e) Xu, L.; Mo, J.; Baillie, C.; Xiao, J. *J. Organomet. Chem.* **2003**, *687*, 310.
13. Machnitzki, P.; Nickel, T.; Stelzer, O.; Landgraf, C. *Eur. J. Inorg. Chem.* **1998**, *7*, 1029.
14. Lauer, M.; Wulff, G. *J. Organomet. Chem.* **1983**, *256*, 1.
15. Martina, S.; Enkelmann, V.; Wegner, G.; Schluter, A.-D. *Synthesis* **1991**, 613.
16. (a) Fernando, S. R. L.; Maharoof, U. S. M.; Deshayes, K. D.; Kinstle, T. H.; Ogawa, M. Y. *J. Am. Chem. Soc.* **1996**, *118*,

5783. (b) Bolm, C.; Ewald, M.; Felder, M.; Schlingloff, G. *Chem. Ber.* **1992**, *125*, 1169.
17. (a) Parrish, C. A.; Buchwald, S. L. *J. Org. Chem.* **2001**, *66*, 3820. (b) Nishimura, M.; Ueda, M.; Miyaura, N. *Tetrahedron* **2002**, *58*, 5779.
18. Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295.
19. (a) Kotha, S.; Lahiri, K.; Kashinath, D. *Tetrahedron* **2002**, *58*, 9633. (b) Majo, V. J.; Prabhakaran, J.; Mann, J. J.; Kumar, J. S. D. *Adv. Synth. Catal.* **2003**, *345*, 620, and references therein.
20. Johnson, C. N.; Stemp, G.; Anand, N.; Stephen, S. C.; Gallagher, T. *Synlett* **1998**, 1025.
21. Gronowitz, S.; Bjork, P.; Malm, J.; Hornfeldt, A.-B. *J. Organomet. Chem.* **1993**, *460*, 127.
22. Gray, M.; Chapell, B. J.; Felding, J.; Taylor, N. J.; Snieckus, V. *Synlett* **1998**, 422.
23. Ogawa, S.; Tajiri, Y.; Furukawa, N. *Bull. Chem. Soc. Jpn* **1991**, *64*, 3182.