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Palladium-catalyzed coupling reactions of bromo-substituted phenylphosphine oxides: a facile route to functionalized arylphosphine ligands

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Dedicated to Professor J.P. Genêt for his significant contributions to the art of organic synthesis

Abstract

The Heck reaction of $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$ ($n = 1–3$) with electron deficient and neutral olefins led to linear olefin-substituted phenylphosphine oxides, whilst the reaction with an electron rich olefin in an ionic liquid solvent resulted in the formation of acetyl variants. The same bromophenylphosphine oxides also reacted with arylboronic acids under normal Suzuki coupling conditions, affording arylated phenylphosphine oxides in excellent yields. Amination and methoxycarbonylation of the bromophenylphosphine oxides by palladium catalysis were also shown to be feasible. Given that free phosphines can be readily derived from phosphine oxides, palladium-catalyzed coupling of $OPR_{3-n}(C_6H_4Br)_n$ (R = alkyl, aryl) should provide a simple, yet versatile, route to functionalized phosphine ligands.

Keywords: Phosphine oxides; Phosphines; Coupling reactions; Palladium catalysis

1. Introduction

Aryl phosphines have been widely employed as highly efficient ligands for various transformations in homogeneous catalysis and asymmetric synthesis [1]. The functionalities on the aryl groups are of particular relevance to catalytic reactions and can serve as a handle for solubility enhancement or attachment onto solids [1,2]. However, the commercial availability of aryl phosphines in terms of structural diversity is limited and there is no simple route to these functionalities. Attempts to achieve functionalization via traditional methods prove difficult due to the poor functional tolerance and the use of moisture- or air-sensitive reagents [3]. In recent years, catalytic methods have emerged, allowing a variety of structurally and electronically diverse phosphines to be accessed more easily and efficiently [4]. For instance, transition metal catalyzed P–C cross coupling has been developed and shown to provide a very useful approach in phosphine synthesis. Thus, phosphines can be prepared by coupling phosphorus substrates containing a P–X bond (X = H, $SnMe_3$, Cl, SiR_3) with aryl and vinyl halides [5–9]. More recently, the palladium-catalyzed phosphination of aryl bromides using triarylphosphines as the phosphinating agents has been described; the reaction proceeds with good functional group tolerance but suffers from low yields [10].

Palladium-catalyzed C–C coupling reactions have widely been used in organic synthesis, and offer an easy access to functionalized arenes [11]. However, this efficient methodology has received less attention in the catalytic synthesis of functionalized phosphines. In 1997, Trost and co-workers first described the functionalization of triphenylphosphine via palladium-catalyzed C–C coupling reactions [12]. A bromotriarylphosphine or its oxide was used as a starting block to couple with terminal alkynes and

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arylboronic acids. It was observed that in the presence of $Pd(PPh_3)_4$, the Suzuki coupling of bromoarylphosphines with phenylboronic acid was sluggish and incomplete due to possible catalyst poisoning. With the corresponding phosphine oxide, however, the Suzuki reaction proceeded smoothly to give the product in high yield. Obviously, the phosphine oxide is advantageous over its free form due to its stability and less likelihood for coordination. The strong electron-withdrawing effect of the phosphoryl moiety should not be overlooked, however (vide infra). Similar observations were made in the coupling reactions with terminal alkynes. After reduction with $HSiCl_3$, the functionalized arylphosphines were obtained in high yields. Focusing their research on polymer-supported catalysts, Pu and his co-workers synthesized polymer-supported BINAP via the Suzuki coupling of a chiral binaphthyl monomer with dibromobenzene followed by $HSiCl_3$ reduction [13]. Buchwald and co-worker described an efficient asymmetric Suzuki cross coupling for the synthesis of new chiral phosphine ligands in high yields and excellent ee values [14]. More recently, palladium-catalyzed Suzuki coupling has been employed by Zhang and co-workers to prepare a multi-substituted BIPHEP ligand [BIPHEP = 2,2′-bis(diphenylphosphino)biphenyl] [15]. Treatment of an iodo-substituted arylphosphine oxide with phenylboronic acid in the presence of $Pd(PPh_3)_4$ led to the formation of a phenyl-substituted arylphosphine oxide. The subsequent copper-mediated Ullmann coupling furnished the BIPHEP ligand in good yield. In addition to Suzuki coupling, the Heck and Stille reactions have been applied to the synthesis of phosphorus compounds [16].

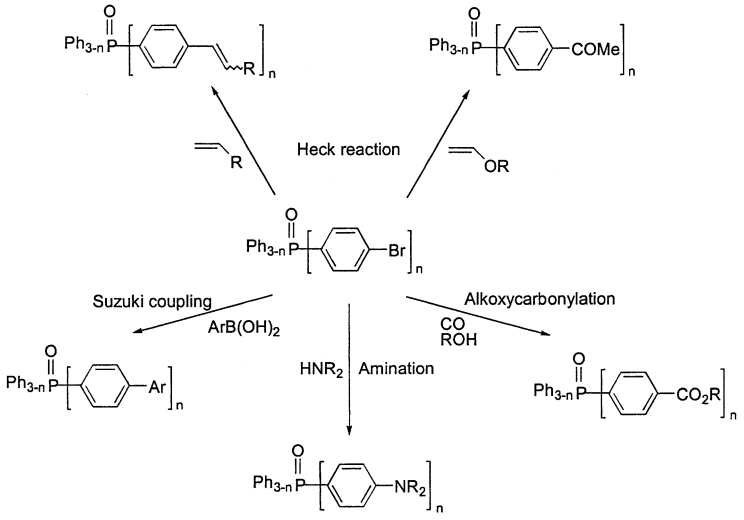
We previously reported a simple and high-yield method for a variety of functionalized arylphosphines by palladium-catalyzed C–C coupling reactions [17]. With the easily available haloarylphosphine oxides $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$ as starting material, phosphines bearing fluoroalkylated chains with CH_2CH_2 spacers, and the alkyl variants including those containing carboxylate groups were synthesized by the Heck arylation of the corresponding olefins; these phosphines can be used as ligands for catalysis in supercritical CO_2, fluorous solvents as well as water. The methodology was further extended to the preparation of functionalized biphenyl phosphines via the Suzuki coupling of $OPPh_2(o\text{-}C_6H_4Br)$ with various arylboronic acids [17c]. In an attempt to determine if palladium catalysis could be applied to the preparation of a wider range of phosphines that may find use in catalysis and organometallic chemistry, we undertook a broader investigation into the palladium-catalyzed reaction of $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$. The results are briefly summarized in Scheme 1 and presented in detail below.

2. Results and discussion

2.1. Synthesis of functionalized arylphosphine oxides by the Heck reaction

The Heck reaction provides a powerful C–C bond forming process in organic synthesis, permitting the coupling of aryl/vinyl halides with a wide array of olefins and introducing an ethylene spacer between the aromatic/vinylic units and substituents at the C=C double bond. In our initial study, we found that tris(4-bromophenyl)phosphine failed to couple with *n*-butyl acrylate under normal Heck conditions with the Herrmann–Beller palladacycle [18] as catalyst in *N*,*N*-dimethylformamide (DMF) at 120 °C for 24 h, possibly partly due to poisoning of active palladium species by the excessive phosphine. Whilst borane protected primary or secondary phosphines have been employed in the synthesis of phosphine ligands [7], the borane-protected tris(4-bromophenyl)phosphine did not react with *n*-butyl acrylate. Because the presence of electron withdrawing groups can facilitate the oxidative addition of aryl halides to active Pd(0) species and the P=O moiety exhibits a strong electron withdrawing effect [3], we attempted the Heck reaction of tris(4-chlorophenyl)phosphine oxide with *n*-butyl acrylate using the palladacycle in DMF at 130 °C for 36 h. Unfortunately, we were unable to obtain a reasonable yield of olefinated phosphine oxide. Even under more forcing conditions, including longer reaction time, higher temperature and increased loading of catalysts, only a very low conversion was observed, suggesting that the palladacycle catalyst is not active enough towards the C–Cl bond under the conditions employed.

A previous ^{1}H-NMR study indicated that the electron-withdrawing effect of the phosphoryl group on the *para* position of a phenyl ring lies between those of a carbonyl and a bromide group [19], and so a P=O substituted phenyl bromide could behave like an activated aryl bromide in the Heck reaction. Indeed, the oxides **1a**–**c** could be easily olefinated with a variety of olefins CH_2=CH–R (R = butoxycarbonyl, cyano, *n*-alkyl, phenyl, 4-chlorophenyl). In a typical coupling reaction, a phosphine oxide was mixed with 1.5 equivalent of an olefin (relative to Br), ca. 1.3 equivalent of NaOAc, and 0.5 mol% of palladacycle catalyst in DMF. The coupling reaction proceeded smoothly at 125 or 130 °C to give the olefinated phosphine oxides **2a**–**k** in high isolated yields (Table 1). Most of the reactions went to completion in 24–30 h reaction time regardless of the number of bromide substitutes in the starting oxide and the nature of olefins. As expected, in the case of *n*-butyl acrylate, styrene and 4-chlorostyrene, substitution of the vinylic protons by the arylphosphine oxides occurred at β carbon of the C=C double bonds leading to *trans* olefins. With acrylonitrile as an olefinating reagent, a

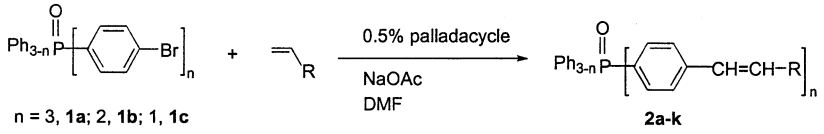


Scheme 1.

higher reaction temperature and longer reaction time was required, and the main products were *trans* olefins with *cis* isomers amounting to about 5–10% as judged by the ^{1}H-NMR spectra. Previously, [Pd(OAc)$_2${P(*o*-Tol)$_3$}$_2$], a precursor to the palladacycle [18], was shown to be highly active in catalyzing the coupling of acrylonitrile with 4-bromobenzaldehyde [20]; but the study also showed the reaction to be strongly substrate-dependent, with electron-withdrawing substituents favoring faster rates, suggesting that the C–Br bond in **1** may not be as activated as that in 4-bromobenzaldehyde. Regioisomers were also produced with the more electron-rich 1-alkenes, where 10% of the product was generated from 2-substitution according to NMR integration.

The Heck reaction can also be extended to the arylation of *n*-butyl vinyl ether with the phosphine oxides. It has been known that with electron-rich acyclic olefins such as enol ethers and enamides, mixtures of regioisomers usually result under normal Heck arylation conditions, due to competing neutral and ionic reaction pathways with one leading to α and the other to β substitution [21]. We recently found that highly regioselective arylation of *n*-butyl vinyl ether could be readily achieved with palladium catalysis when the reaction was carried out in an ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF$_4$]); the reaction uses aryl halides instead of the commonly used, but commercially unavailable aryl triflates [22]. More recently, Hallberg and co-workers reported that similar reactions

Table 1
Heck coupling of OPPh$_{3-n}$(4-C$_6$H$_4$Br)$_n$ with CH$_2$=CH–R



n = 3, **1a**; 2, **1b**; 1, **1c** — **2a-k**

Entry	R	*n*	Product	Temperature (°C)	Time (h)	Yield (%)
1	CO_2Bu	3	**2a**	125	24	98
2	CO_2Bu	2	**2b**	125	20	95
3	CO_2Bu	1	**2c**	125	20	98
4	CN	3	**2d**	130	30	74
5	CN	2	**2e**	130	30	85
6	CN	1	**2f**	130	24	91
7	*n*-C_4H_9	3	**2g**	125	24	92
8	*n*-C_8H_{17}	3	**2h**	125	24	93
9	*n*-$C_{14}H_{29}$	3	**2i**	125	24	86
10	Ph	3	**2j**	125	24	91
11	4-Cl–Ph	3	**2k**	125	24	89

See Section 4 for details of reaction conditions and product analysis.

could be effected when a mixture of DMF/water was used as solvent [23]. In continuing our interest of catalysis in ionic liquids [22,24], we thought that the ionic environment generated from an ionic liquid such as [bmim][BF_4] might also promote the regioselective functionalization of haloarylphosphine oxides. The arylation of *n*-butyl vinyl ether by **1a** was first examined in [bmim][BF_4] under the previously established reaction conditions, where the active catalyst was generated in situ from $Pd(OAc)_2$ and two equivalents of 1,3-bis(diphenylphosphino)propane (DPPP). The oxide **1a** did react with the butyl vinyl ether to give preferentially the α arylated product, although the conversion was only about 30% at 100 °C after 24 h. The β product was not detected by NMR. On the basis of this initial study, the bromides **1a**–**c** were olefinated with *n*-butyl vinyl ether at a higher temperature, 125 °C, in [bmim][BF_4]. As shown in Table 2, the acetyl substituted phosphine oxides **3a**–**c** were obtained in good yields after acidification with HCl.

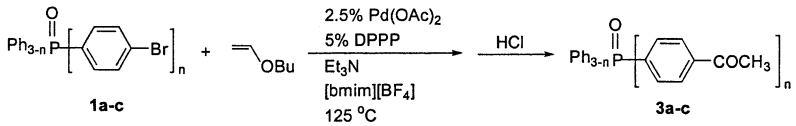
2.2. Synthesis of functionalized arylphosphine oxides by Suzuki coupling

The Suzuki coupling is one of the most powerful tools for the synthesis of biaryls, but has rarely been employed for the direct preparation of phosphine ligands (vide ante) [4]. In general, Suzuki reactions can be more easily performed with aryl bromides and iodides than with aryl chlorides. Indeed, despite the presence of electron-withdrawing P=O moiety, tris(4-chlorophenyl)phosphine oxide was inactive towards arylboronic acids under normal Suzuki reaction conditions. Our recent investigation shows that arylboronic acids can be readily coupled with $OPPh_2(o\text{-}C_6H_4Br)$ under palladium catalysis, providing an easy entry to functionalized biphenyl-based phosphines [17c]. Bearing this success in mind, we attempted the coupling of **1a**–**c** with arylboronic acids. The coupling reaction was carried out with **1**, 1.1 equivalent of an arylboronic acid, two equivalents of a base (relative to Br) in 1,4-dioxane at 105 °C. The palladium catalyst was generated in situ from $Pd_2(dba)_3$ and four equivalents of PPh_3, which was chosen as the ligand due to its ready availability and ease of handling. Table 3 summaries the results obtained. As can be seen, the aryl bromides **1a**–**c** coupled readily with phenylboronic acids and other substituted phenylboronic acids to give the biaryls in excellent yields regardless of the number of bromides in **1** and the nature of the substituents at arylboronic acids. However, when tris(4-bromophenyl)phosphine was employed as substrate, the coupling reaction became sluggish, yielding very low conversion, which is reminiscent of the Heck reaction discussed above and in line with Trost's observation [12]. This efficient coupling process could thus be used to prepare aromatic phosphines with interesting structures and electronic properties. Compounds **4a**–**c** have previously been made by lithiation and other methods [25].

2.3. Synthesis of functionalized arylphosphine oxides by amination

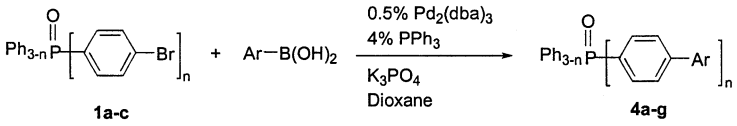
Owing to the excellent studies by the research groups of Buchwald and Hartwig, the palladium-catalyzed amination of aryl halides has been under intensive research in recent years [11]. Among the ligands employed in the amination, Nolan and co-workers found that the readily available, nucleophilic *N*-heterocyclic carbenes, an alternative to electron-rich phosphines [26], displayed good performance in palladium-catalyzed amination of aryl halides [27]. Using Nolan's conditions, we carried out the amination of aryl bromides **1a**–**c** in the presence of palladium and the bulky carbene precursor, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPrHCl) [28]. A typical reaction consisted of simply heating a mixture of substrates, $Pd_2(dba)_3$, IPrHCl and KO^{t}Bu in dioxane under an atmosphere of argon. All the reactions went to completion in 20–24 h. The results are summarized in Table 4. As shown, oxides **1a**–**c** could be easily aminated by *N*-methylaniline in good yields. Due to the easy availability and diversity of amines, this process offers another route to functionalized phosphine ligands, for example, those

Table 2
Heck coupling of $OPPh_{3-n}(4\text{-}C_6H_4\text{–}Br)_n$ with CH_2=CH–O–Bu



Entry	*n*	Product	Time (h)	Yield (%)
1	3	**3a**	30	52
2	2	**3b**	24	70
3	1	**3c**	24	80

Table 3
Suzuki coupling of $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$ with arylboronic acids



Entry	Ar	*n*	Product	Temperature (°C)	Time (h)	Yield
1	Ph	3	**4a**	100	20	91
2	Ph	2	**4b**	100	20	96
3	Ph	1	**4c**	100	20	96
4	$4\text{-}CH_3\text{–}C_6H_4$	3	**4d**	110	24	91
5	$4\text{-}CH_3\text{–}C_6H_4$	1	**4e**	110	24	90
6	$4\text{-}CH_3O\text{–}C_6H_4$	1	**4f**	110	24	89
7	$4\text{-}F\text{–}C_6H_4$	1	**4g**	110	24	91

that could be made water-soluble upon quaternization or are immobilizable through hydrogen bonding with surface hydroxyl groups.

2.4. Synthesis of functionalized arylphosphine oxides by alkoxycarbonylation

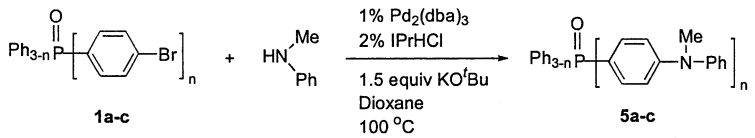
Palladium-catalyzed alkoxycarbonylation of aryl halides provides a facile route for the introduction of carboxylate groups [11a,b]. Due to the activating effect of phosphoryl, we envisaged that the carbonylation of **1a**–**c** could be easily conducted. Indeed, the reactions of the oxides **1a**–**c** with CO and methanol in the presence of $PdCl_2$, PPh_3 and triethylamine in DMF proceeded smoothly to give excellent yields of carbonylated products, although the tris-brominated **1a** required a longer reaction time for complete conversion than **1c** (Table 5).

This reaction offers a most convenient method for the synthesis of carbonylated phosphine ligands. Traditionally, the synthesis of **6** involves the use of stoichiometric Grignard/lithium reagents, or a large excess of oxidant, and none are catalytic in nature [29]. Recently, Hayashi [8a] and Saa [6f] reported the synthesis of **6c** in high yield by palladium catalysed P–C coupling reaction of aryl triflates with diphenylphosphine oxide. Using our palladium-catalyzed carbonylation route, the phosphines can now be more easily accessed considering that triflates are in general not commercially available and secondary phosphines are often pyrophoric. Phosphine oxides such as **6** can be used not only as precursors to amphiphilic ligands [17b] but also as monomers to fire resistant polymers [29].

3. Conclusions

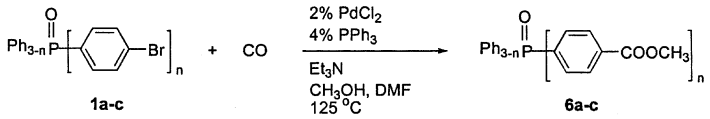
The results presented in this paper demonstrate that palladium catalysis provides a simple, but powerful, tool for the preparation of a wide range of arylphosphine compounds. The substrates can be selected such that the phosphine products display designer electronic or solubility properties, and are amenable to further functionalization or immobilization on solids. Specifically, we

Table 4
Amination of $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$ with *N*-methylaniline



Entry	*n*	Product	Time (h)	Yield (%)
1	3	**5a**	24	51
2	2	**5b**	20	71
3	1	**5c**	20	79

Table 5
Methoxycarbonylation of $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$



Entry	*n*	Product	Time (h)	Yield (%)
1	3	**6a**	24	90
2	2	**6b**	20	92
3	1	**6c**	12	92

have demonstrated that the widely-practiced, palladium-catalyzed Heck reaction, Suzuki coupling, Buchwald–Hartwig amination and alkoxycarbonylation can be readily adopted to the preparation of olefinated, arylated, aminated and carbonylated phenylphosphines. These reactions are easy to conduct, with common ligands being sufficiently effective to give good to excellent yields.

4. Experimental

All reactions were performed under an inert atmosphere and anhydrous conditions. ^{1}H- and ^{13}C-NMR spectra were obtained on a Varian Gemini 300 or a Bruker Avance 400 spectrometer in $CDCl_3$ with Me_4Si as internal standard. $^{31}P\{^1H\}$-NMR spectra were recorded on a Bruker WM 250 spectrometer in $CDCl_3$ with 85% H_3PO_4 as external standard. Elemental analysis was performed by the Microanalysis Laboratory, Department of Chemistry, University of Liverpool. Mass spectra were obtained by electron ionization (EI) recorded on a VG7070E mass spectrometer. Silica gel (Daiso gel IR-60) was used for column chromatography. 1,4-Dioxane was distilled over Na/benzophenone under nitrogen. DMF and NEt_3 were distilled under nitrogen over CaH_2 and stored over activated 4A molecular sieves. Commercial deuterated chloroform for NMR spectroscopy and solvents for chromatography were used without further purification. Olefins, arylboronic acids, *N*-methylaniline, potassium *tert*-butoxide, $PdCl_2$, $Pd(OAc)_2$, $Pd_2(dba)_3$, PPh_3 and DPPP were purchased from Aldrich and Lancaster, and used without further purification. 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) [30] and IPrHCl [28] were prepared according to published procedures; so were the bromophenylphosphine oxides $OPPh_{3-n}(4\text{-}C_6H_4Br)_n$ ($n = 3$, **1a**; 2, **1b**; 1, **1c**) [19] and the Herrmann–Beller palladacycle catalyst [18].

4.1. Tris[4-(2-butoxycarbonylvinyl)phenyl]phosphine oxide (2a)

A mixture of tris(4-bromophenyl)phosphine oxide **1a** (2.060 g, 4.0 mmol), *n*-butyl acrylate (2.307 g, 18 mmol), palladacycle (56 mg, 0.06 mmol) and NaOAc (1.312 g, 16 mmol) in DMF (50 ml) was stirred for 24 h at 125 °C. After cooling to ambient temperature, most of the DMF was removed under reduced pressure. The residue was dissolved in $CHCl_3$ (50 ml), washed with water (2 × 50 ml) and brine (50 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography (EtOAc/$CHCl_3$ = 1/4) to give **2a** as white crystals (2.602 g, 98%). ^{1}H-NMR (300 MHz, $CDCl_3$, Me_4Si): $\delta = 0.97$ (t, ^3J(H, H) = 7.2 Hz, 9H), 1.43 (m, 6H), 1.69 (m, 6H), 4.25 (t, ^3J(H, H) = 6.6 Hz, 6H), 6.52 (d, ^3J(H, H) = 16.1 Hz, 3H), 7.61–7.73 (m, 15H); $^{13}C\{^1H\}$-NMR (75 MHz, $CDCl_3$): $\delta = 13.7$, 19.2, 30.7, 64.7, 121.2, 128.1 (d, ^3J(C, P) = 12.5 Hz), 132.6 (d, ^2J(C, P) = 9.8 Hz), 133.7 (d, ^1J(C, P) = 103.7 Hz), 138.4, 142.9, 166.6; $^{31}P\{^1H\}$-NMR ($CDCl_3$): $\delta = 27.3$ (s); MS (EI), *m*/*z* (%): 656 (M^+, 23); Anal. Calc. for $C_{39}H_{45}O_7P$: C, 71.32; H, 6.91. Found: C, 71.27; H, 6.88%.

4.2. Bis[4-(2-butoxycarbonylvinyl)phenyl]-phenylphosphine oxide (2b)

The procedure was similar to that for **2a**; **2b** was obtained as colorless oil in 95% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.95 (t, ^3J(H, H) = 7.5 Hz, 6H), 1.42 (m, 4H), 1.68 (m, 4H), 4.21 (t, ^3J(H, H) = 6.7 Hz, 4H), 6.56 (d, ^3J(H, H) = 16.1 Hz, 2H), 7.44–7.76 (m, 15H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ 14.0, 19.4, 30.7, 64.9, 121.2, 128.3 (d, ^3J(C, P) = 12.5 Hz), 129.0 (d, ^3J(C, P) = 12.0 Hz), 132.0 (d, ^1J(C, P) = 104.6 Hz), 132.2 (d, ^2J(C, P) = 9.9 Hz), 132.6, 132.8 (d, ^2J(C, P) = 10.1 Hz), 134.2 (d, ^1J(C, P) = 103.1 Hz), 138.3, 143.2, 166.7; ^{31}P-NMR (101 MHz, $CDCl_3$) δ 28.3 (s); MS (EI), *m*/*z* (%): 530 (M^+, 79), 531 (25), 532 (7), 529 (100); Anal. Calc. for $C_{32}H_{35}O_5P$: C, 72.44; H, 6.65. Found: C, 72.66; H, 6.55%.

4.3. [4-(2-butoxycarbonylvinyl)phenyl]-diphenylphosphine oxide (**2c**)

The procedure was similar to that for **2a**; **2c** was obtained as colorless oil in 98% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 0.96 (t, ^3J(H, H) = 7.5 Hz, 3H), 1.42 (m, 2H), 1.69 (m, 2H), 4.22 (t, ^3J(H, H) = 6.6 Hz, 2H), 6.51 (d, ^3J(H, H) = 16.1 Hz, 1H), 7.44–7.49 (m, 4H), 7.53–7.59 (m, 4H), 7.65–7.72 (m, 7H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 13.7, 19.2, 30.8, 64.7, 120.8, 127.8 (d, ^3J(C, P) = 12.7 Hz), 128.6 (d, ^3J(C, P) = 12.5 Hz), 132.0 (d, ^2J(C, P) = 9.5 Hz), 132.1, 132.3 (d, ^1J(C, P) = 104.0 Hz), 132.6 (d, ^2J(C, P) = 10.3 Hz), 134.6 (d, ^1J(C, P) = 102.4 Hz), 137.9, 143.1, 166.5; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 29.5 (s); MS (EI), *m*/*z* (%): 404 (M^+, 53), 403 (100), 405 (13); Anal. Calc. for $C_{25}H_{25}O_3P$: C 74.24; H, 6.23. Found: C, 73.93; H, 6.21%.

4.4. Tris[4-(2-cyanovinyl)phenyl]phosphine oxide (**2d**)

A mixture of **1a** (2.060 g, 4.0 mmol), acrylonitrile (1.273 g, 24 mmol), palladacycle (56 mg, 0.06 mmol), and NaOAc (1.182 g, 14 mmol) in DMF (50 ml) was stirred for 30 h at 130 °C. After cooling to ambient temperature the mixture was poured into water (50 ml). The product was extracted with $CHCl_3$ (3 × 30 ml). The combined organic layers were washed with water (2 × 50 ml) and brine (50 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography (EtOAc/$CHCl_3$ = 1/4) and crystallized from EtOAc to give **2d** as white crystals (1.276 g, 74%). ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 5.61 (d, ^3J(H, H) = 12.1 Hz, 0.3H, *Z* isomer), 5.99 (d, ^3J(H, H) = 16.7 Hz, 2.7H, *E* isomer), 7.19 (d, ^3J(H, H) = 12.1 Hz, 0.3H, *Z* isomer), 7.43(d, ^3J(H, H) = 16.7 Hz, 2.7H, *E* isomer), 7.57 (dd, ^3J(H, H) = 8.2 Hz, ^4J(P, H) = 2.4 Hz, 6H), 7.71 (dd, ^3J(P, H) = 11.7 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 100.1, 117.6, 127.8 (d, ^3J(C, P) = 12.4 Hz), 133.1 (d, ^2J(C, P) = 10.3 Hz), 134.8 (d, ^1J(C, P) = 104.1 Hz), 137.6, 149.1; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 26.9 (s); MS (EI), *m*/*z* (%): 431 (M^+, 75), 430 (100), 432 (20); Anal. Calc. for $C_{27}H_{18}N_3OP$: C, 75.17; H, 4.21; N, 9.74. Found: C, 75.13; H, 4.17; N, 9.70%.

4.5. Bis[4-(2-cyanovinyl)phenyl]phenylphosphine oxide (**2e**)

The procedure was similar to that for **2d**; **2e** was obtained as white crystals in 85% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 5.60 (d, ^3J(H, H) = 12.0 Hz, 0.1H, *Z* isomer), 5.99 (d, ^3J(H, H) = 16.6 Hz, 1.9H, *E* isomer), 7.18 (d, ^3J(H, H) = 12.2 Hz, 0.1H, *Z* isomer), 7.42 (d, ^3J(H, H) = 16.7 Hz, 1.9H, *E* isomer), 7.49–7.90 (m, 13H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ 99.7, 117.7, 127.7 (d, ^3J(C, P) = 12.7 Hz), 129.2 (d, ^3J(C, P) = 11.9 Hz), 131.7, 132.3 (d, ^2J(C, P) = 10.3 Hz), 133.1 (d, ^2J(C, P) = 10.3 Hz), 133.4 (d, ^1J(C, P) = 102.1 Hz), 135.5 (d, ^1J(C, P) = 102.4 Hz), 137.3, 149.4; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 28.3 (s); MS (EI), *m*/*z* (%): 380 (M^+, 64), 379 (100), 381 (15); Anal. Calc. for $C_{24}H_{17}N_2OP$: C, 75.78; H, 4.50; N, 7.36. Found: C, 75.63; H, 4.59; N, 7.19%.

4.6. [4-(2-cyanovinyl)phenyl]diphenylphosphine oxide (**2f**)

The procedure was similar to that for **2d**; **2f** was obtained as white crystals in 91% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 5.59 (d, ^3J(H, H) = 12.1 Hz, 0.05H, *Z* isomer), 5.99 (d, ^3J(H, H) = 16.7 Hz, 0.95H, *E* isomer), 7.19 (d, ^3J(H, H) = 12.1 Hz, 0.05H, *Z* isomer), 7.43 (d, ^3J(H, H) = 16.7 Hz, 0.95H, *E* isomer), 7.46–7.51 (m, 4H), 7.53–7.60 (m, 4H), 7.64–7.75 (m, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 99.4, 118.0, 127.6 (d, ^3J(C, P) = 11.9 Hz), 129.1 (d, ^3J(C, P) = 11.9 Hz), 132.2 (d, ^1J(C, P) = 104.8 Hz), 132.4 (d, ^2J(C, P) = 10.3 Hz), 132.7, 133.2 (d, ^2J(C, P) = 9.5 Hz), 136.2 (d, ^1J(C, P) = 101.6 Hz), 137.0, 149.6; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 29.1 (s); MS (EI), *m*/*z* (%): 329 (M^+, 49), 328 (100), 330 (10); Anal. Calc. for $C_{21}H_{16}NOP$: C, 76.59; H, 4.90; N, 4.25. Found: C, 76.39; H, 4.92; N, 4.25%.

4.7. Tris[4-(1-hexenyl)phenyl]phosphine oxide (**2g**)

The procedure was similar to that for **2a** except nine equivalents (relative to phosphorus) of 1-hexene was used. After purification by flash chromatography ($CHCl_3$), **2g** was obtained as colorless oil in 92% yield, which contained 10% of tris[4-(2-hexenyl)phenyl]phosphine oxide. ^{1}H-NMR (300 MHz, $CDCl_3$, Me_4Si): δ 0.92 (t, ^3J(H, H) = 7.2 Hz, 9H), 1.41 (m, 12H), 2.23 (m, 6H), 6.38 (m, 6H), 7.40 (dd, ^3J(H, H) = 7.9 Hz, ^4J(P, H) = 2.4 Hz, 6H), 7.58 (dd, ^3J(P, H) = 11.5 Hz, ^3J(H, H) = 7.9 Hz, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 13.9, 22.2, 31.3, 32.8, 125.9 (d, ^3J(C, P) = 12.1 Hz), 129.04, 130.82 (d, ^1J(C, P) = 105.9 Hz), 132.42 (d, ^2J(C, P) = 10.4 Hz), 134.16, 141.46; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 28.6 (s); MS (EI), *m*/*z* (%): 524 (M^+, 100), 523 (94), 526 (35), 540 (9); Anal. Calc. for $C_{36}H_{45}OP$: C, 82.40; H, 8.64. Found: C, 82.27; H, 8.73%.

4.8. Tris[4-(1-decenyl)phenyl]phosphine oxide (**2h**)

The procedure was similar to that for **2a** except 4.5 equivalents (relative to phosphorus) of 1-decene was used. After purification by flash chromatography ($CHCl_3$), **2h** was obtained as colorless oil in 93% yield, which contained 10% tris[4-(2-decenyl)phenyl]phosphine oxide. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.85 (t, ^3J(H, H) = 7.0 Hz, 9H), 1.23 (br, 36H), 2.12–2.38 (m, 6H), 6.39 (m, 6H), 7.36–7.61 (m, 12H); ^{31}P-NMR (101 MHz, $CDCl_3$):

δ 30.8 (s); MS (EI), *m/z* (%): 693(M^+, 49), 635 (10), 555(100); Anal. Calc. for $C_{48}H_{69}OP$: C, 83.19; H, 10.03. Found: C, 82.86; H, 10.00%.

4.9. Tris[4-(1-hexadecenyl)phenyl]phosphine oxide (**2i**)

The procedure was similar to that for **2a** except four equivalents (relative to phosphorus) of 1-hexadecene was used; **2i** was obtained as colorless oil in 86% yield, which contained about 10% of tris[4-(2-hexadecenyl)phenyl]phosphine oxide. ^{1}H-NMR (300 MHz, $CDCl_3$, Me_4Si): 0.88 (t, ^3J(H, H) = 7.0 Hz, 9H), 1.24 (br, 72H), 2.05–2.35 (m, 6H), 6.39 (m, 6H), 7.42–7.60 (m, 12H); ^{31}P-NMR (101 MHz, $CDCl_3$): δ 30.8 (s); MS (FAB), *m/z* (%): 946 (M^+ +1, 62), 962 (100), 978 (83), 994 (42); Anal. Calc. for $C_{66}H_{105}OP$: C, 83.84; H, 11.19. Found: C, 84.07; H, 11.27%.

4.10. Tris[4-(trans-styryl)phenyl)]phosphine oxide (**2j**)

The procedure was similar to that for **2a**; **2j** was obtained as white crystals in 91% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 7.12 (d, ^3J(H, H) = 16.4 Hz, 3H), 7.21 (d, ^3J(H, H) = 16.4 Hz, 3H), 7.22–7.30 (m, 3H), 7.37 (dd, ^3J(H, H) = 7.4 Hz, ^3J(P, H) = 7.4 Hz, 6H), 7.52 (d, ^3J(H, H) = 7.8 Hz, 6H), 7.60 (d, ^3J(H, H) = 7.5 Hz, 6H), 7.67–7.71 (m, 6H); ^{31}P-NMR (101 MHz, $CDCl_3$): δ 29.6 (s); MS (EI), *m/z* (%): 584 (M^+, 81), 583 (51), 585 (31); Anal. Calc. for $C_{42}H_{33}OP$: C, 86.28; H, 5.69. Found: C, 86.17; H, 5.68%.

4.11. Tris[4-(trans-4-chlorostyryl)phenyl]phosphine oxide (**2k**)

The procedure was similar to that for **2a**; **2k** was obtained as white crystals in 89% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 7.07 (d, ^3J(H, H) = 16.4 Hz, 3H), 7.14 (d, ^3J(H, H) = 16.4 Hz, 3H), 7.33 (d, ^3J(H, H) = 8.4 Hz, 6H), 7.44 (d, ^3J(H, H) = 8.6 Hz, 6H), 7.58 (d, ^3J(H, H) = 8.6 Hz, 6H), 7.68 (dd, ^3J(H, H) = 8.3, ^3J(P, H) = 11.4 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 126.9 (d, ^3J(C, P) = 12.7 Hz), 128.3, 128.4, 129.4, 130.4, 132.0 (d, ^1J(C, P) = 105.6 Hz), 132.9 (d, ^2J(C, P) = 10.3 Hz), 134.3, 135.6, 141.0; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 29.4; MS (EI), *m/z* (%): 688 (M^+, 23), 689 (13), 690 (9), 687 (23), 686 (23), 685 (17); Anal. Calc. for $C_{42}H_{30}Cl_3OP$: C, 73.32; H, 4.39. Found: C, 72.98; H, 4.61%.

4.12. Tris(4-acetylphenyl)phosphine oxide (**3a**) [31]

A mixture of **1a** (515 mg, 1.0 mmol), *n*-butyl vinyl ether (1.502 g, 15 mmol), $Pd(OAc)_2$ (17 mg, 0.075 mmol), DPPP (62 mg, 0.15 mmol), triethylamine (456 mg, 4.5 mmol) and [bmim][BF_4] (5 ml) was stirred for 24 h at 125 °C. At room temperature HCl (5%, 15 ml) was added and, after 0.5 h of stirring, the product was extracted with $CHCl_3$ (3 × 15 ml). The combined organic layers were washed with water (2 × 30 ml) and brine (30 ml), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography (EtOAc/hexane = 40/1) to give **3a** as colorless oil (210 mg, 52%). ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 2.64 (s, 9H), 7.79 (dd, ^3J(H, H) = 8.3 Hz, ^3J(P, H) = 11.1 Hz, 6H), 8.05 (d, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 26.8, 128.3 (d, ^3J(C, P) = 11.9 Hz), 132.4 (d, ^2J(C, P) = 10.3 Hz), 136.4 (d, ^1J(C, P) = 101.6 Hz), 140.1, 197.2; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 27.8 (s); MS (EI), *m/z* (%): 404 (M^+, 59), 403 (100), 405 (12); Anal. Calc. for $C_{24}H_{21}O_4P$: C, 71.28; H, 5.23. Found: C, 71.52; H, 5.13%.

4.13. Bis(4-acetylphenyl)phenylphosphine oxide (**3b**) [31]

The procedure was similar to that for **3a** except ten equivalents (relative to phosphorus) of *n*-butyl vinyl ether was used; **3b** was obtained as colorless oil in 70% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 2.63 (s, 6H), 7.48–7.68 (m, 5H), 7.79 (dd, ^3J(H, H) = 8.4 Hz, ^3J(P, H) = 11.6 Hz, 4H), 8.03 (dd, ^4J(P, H) = 2.4 Hz, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 27.1, 128.5 (d, ^3J(C, P) = 11.9 Hz), 129.2 (d, ^3J(C, P) = 11.9 Hz), 131.6 (d, ^1J(C, P) = 104.8 Hz), 132.4 (d, ^2J(C, P) = 10.3 Hz), 132.8 (d, ^2J(C, P) = 10.3 Hz), 133.0, 137.4 (d, ^1J(C, P) = 100.1 Hz), 140.2, 197.7; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 28.6 (s); MS (EI), *m/z* (%): 362 (M^+, 47), 361 (100), 362 (7); Anal. Calc. for $C_{22}H_{19}O_3P$: C, 72.92; H, 5.28. Found: C, 73.02; H, 5.25%.

4.14. (4-Acetylphenyl)diphenylphosphine oxide (**3c**) [31]

The procedure was similar to that for **3a** except five equivalents (relative to phosphorus) of *n*-butyl vinyl ether was used; **3c** was obtained as colorless oil in 80% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 2.62 (s, 3H), 7.46–7.69 (m, 10H), 7.80 (dd, ^3J(H, H) = 8.6 Hz, ^3J(P, H) = 11.3 Hz, 2H), 8.02 (dd, ^4J(P, H) = 2.0 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 27.1, 128.4 (d, ^3J(C, P) = 12.7 Hz), 129.0 (d, ^3J(C, P) = 12.7 Hz), 132.4 (d, ^2J(C, P) = 9.5 Hz), 132.6, 132.8 (d, ^2J(C, P) = 10.3 Hz), 139.9, 197.8; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 29.4 (s); MS (EI), *m/z* (%): 320 (M^+, 41), 319 (100); Anal. Calc. for $C_{20}H_{17}O_2P$: C, 74.99; H, 5.35. Found: C, 75.12; H, 5.28%.

4.15. Tris(4-biphenylyl)phosphine oxide (**4a**) [25a]

A mixture of **1a** (2.060 g, 4.0 mmol), phenylboronic acid (1.609 g, 13 mmol), $Pd_2(dba)_3$ (55 mg, 0.06 mmol), PPh_3 (126 mg, 0.48 mmol) and K_3PO_4 (5.095 g, 24

mmol) in 1,4-dioxane (50 ml) was stirred overnight at 100 °C. After cooling to room temperature, the mixture was diluted with water 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 product was purified by flash chromatography ($CHCl_3$) and crystallized in EtOAc as white crystals (1.84 g, 91%). ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 7.34–7.41 (m, 3H), 7.44–7.48 (m, 6H), 7.62 (d, ^3J(H, H) = 7.4 Hz, 6H), 7.72 (d, ^3J(H, H) = 7.4 Hz, 6H), 7.80–7.85 (m, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 127.3 (d, ^2J(C, P) = 9.3 Hz), 128.2, 129.0, 131.4 (d, ^1J(C, P) = 105.4 Hz), 132.7(d, ^3J(C, P) = 9.8 Hz), 140.0, 144.9; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 29.8 (s); MS (EI), *m*/*z* (%): 506 (83, M^+), 507 (25), 505 (97), 429 (14), 351 (17), 337 (39), 306 (21); Anal. Calc. for $C_{36}H_{27}OP$: C, 85.36; H, 5.37. Found: C, 85.07; H, 5.41%.

4.16. Bis(4-biphenylyl)phenylphosphine oxide (**4b**)

The procedure was similar to that for **4a**; **4b** was obtained as white crystal in 96% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 7.36–7.41(m, 2H), 7.44–7.52 (m, 6H), 7.55–7.62 (m, 5H), 7.70 (dd, ^3J(H, H) = 8.4 Hz, ^4J(H, H) = 2.7 Hz, 4H), 7.73–7.81 (m, 6H); ^{31}P-NMR (101 MHz, $CDCl_3$): δ 29.8 (s); MS (EI), *m*/*z* (%): 430 (M^+, 64), 429 (100), 431 (18); Anal. Calc. for $C_{30}H_{23}OP$: C, 83.70; H, 5.39. Found: C, 84.00; H, 5.44%.

4.17. (4-Biphenylyl)diphenylphosphine oxide (**4c**) [25b]

The procedure was similar to that for **4a**; **4c** was obtained as white crystal in 96% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 7.36–7.40 (m, 1H), 7.43–7.49 (m, 6H), 7.53–7.61 (m, 4H), 7.65–7.76 (m, 8H); ^{31}P-NMR (101 MHz, $CDCl_3$): δ 30.1 (s); MS (EI), *m*/*z* (%): 354 (M^+, 55), 353 (100), 355 (11); Anal. Calc. for $C_{24}H_{19}OP$: C, 81.34; H, 5.40. Found: C, 81.39; H, 5.39%.

4.18. Tris[4-(4-tolyl)phenyl]phosphine oxide (**4d**)

The procedure was similar to that for **4a**; **4d** was obtained as white crystal in 91% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 2.40 (s, 9H), 7.26 (d, ^3J(H, H) = 7.8 Hz, 6H), 7.51 (d, 6H), 7.69 (dd, ^3J(H, H) = 8.3 Hz, ^4J(P, H) = 2.5 Hz, 6H), 7.79 (dd, ^3J(P, H) = 11.6 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 21.5, 127.4 (d, ^3J(C, P) = 11.9 Hz), 127.5, 130.1, 131.4 (d, ^1J(C, P) = 105.6 Hz), 133.0 (d, ^2J(C, P) = 10.3 Hz), 137.5, 138.5, 145.1; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 29.9 (s); MS (EI), *m*/*z* (%): 548 (M^+, 93), 547 (100), 549 (30), 550 (6); HRMS Calc. for $C_{39}H_{33}OP$ [M^+]: 548.22693; Found: 548.22885; Anal. Calc. for $C_{39}H_{33}OP$: C, 85.38; H, 6.06. Found: C, 85.61; H, 5.98%.

4.19. [4-(4-Tolyl)phenyl]diphenylphosphine oxide (**4e**)

The procedure was similar to that for **4a**; **4e** was obtained as white crystal in 90% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 2.40 (s, 3H), 7.27 (d, ^3J(H, H) = 8.4 Hz, 2H), 7.44–7.58 (m, 8H), 7.64–7.76 (m, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 21.2, 127.0 (d, ^3J(C, P) = 12.7 Hz), 127.1, 128.5 (d, ^3J(C, P) = 12.9 Hz), 129.7, 130.8 (d, ^1J(C, P) = 103.1 Hz), 131.9, 132.2 (d, ^2J(C, P) = 9.5 Hz), 132.3, 132.6 (d, ^2J(C, P) = 10.0 Hz), 132.8 (d, ^1J(C, P) = 104.0 Hz), 138.2, 144.7; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 30.1 (s); MS (EI), *m*/*z* (%): 368 (M^+, 64), 367 (100), 369 (14); Anal. Calc. for $C_{25}H_{21}OP$: C, 81.50; H, 5.75. Found: C, 81.33; H, 5.73%.

4.20. [4-(4-Methoxyphenyl)phenyl]diphenylphosphine oxide (**4f**)

The procedure was similar to that for **4a**; **4f** was obtained as white crystal in 89% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 3.85 (s, 3H), 6.98 (m, 2H), 7.34–7.48 (m, 4H), 7.52–7.57 (m, 4H), 7.64–7.74 (m, 8H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 55.4, 114.5, 127.1 (d, ^3J(C, P) = 11.9 Hz), 128.4, 128.5 (d, ^3J(C, P) = 11.9 Hz), 130.4 (d, ^1J(C, P) = 104.8 Hz), 131.9, 132.1(d, ^2J(C, P) = 9.5 Hz), 132.6 (d, ^2J(C, P) = 10.3 Hz), 132.9 (d, ^1J(C, P) = 102.4 Hz), 144.3, 159.9; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 30.1; MS (EI), *m*/*z* (%): 384 (M^+, 71), 383 (100), 385 (15), 307 (11); Anal. Calc. for $C_{25}H_{21}O_2P$: C, 78.11; H, 5.51. Found: C, 78.20; H, 5.51%.

4.21. [4-(4-Fluorophenyl)phenyl]diphenylphosphine oxide (**4g**)

The procedure was similar to that for **4a**; **4g** was obtained as white crystals in 91% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 7.15 (dd, ^3J(H, H) = 8.7 Hz, ^3J(H, F) = 8.7 Hz, 2H), 7.46–7.50 (m, 4H), 7.54–7.59 (m, 4H), 7.63 (dd, ^3J(H, H) = 8.1 Hz, ^4J(P, H) = 2.0 Hz, 2H), 7.69–7.76 (m, 6H); ^{31}P-NMR (101 MHz, $CDCl_3$): δ 29.9 (s); MS (EI), *m*/*z* (%): 372 (M^+, 56), 371 (100), 373 (12); Anal. Calc. for $C_{24}H_{18}OFP$: C, 77.41; H, 4.87. Found: C, 77.70; H, 4.83%.

4.22. Tris[4-(N-methyl-N-phenylamino)phenyl]-phosphine oxide (**5a**)

A mixture of **1a** (2.060 g, 4.0 mmol), *N*-methylaniline (1.543 g, 14 mmol), $Pd_2(dba)_3$ (110 mg, 0.12 mmol), IPrHCl (103 mg, 0.24 mmol) and KO^{t}Bu (2.02 g, 18 mmol) in 1,4-dioxane (50 ml) was stirred for 24 h at 100 °C. After cooling to room temperature, the mixture was diluted with water 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

product was purified by flash chromatography (EtOAc/$CHCl_3$ = 1/2) to give **5a** as yellow oil (1.21g, 51%). ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 3.32 (s, 9H), 6.81 (dd, ^3J(H, H) = 8.9 Hz, ^4J(P, H) = 2.2 Hz, 6H), 7.11–7.17 (m, 9H), 7.32–7.37 (m, 6H), 7.46 (dd, ^3J(P, H) = 11.3 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 40.1, 114.8 (d, ^3J(C, P) = 12.5 Hz), 122.0 (d, ^1J(C, P) = 112.0 Hz), 124.7, 125.2, 129.7, 133.4 (d, ^2J(C, P) = 11.0 Hz), 147.8, 151.3; ^{31}P-NMR (101 MHz, $CDCl_3$) δ 30.6; MS (EI), *m/z* (%): 593 (M^+, 100), 594 (36), 595 (7), 592 (80), 411 (14), 409 (19), 395 (30); Anal. Calc. for $C_{39}H_{36}N_3OP$: C, 78.90; H, 6.11; N, 7.08. Found: C, 78.55; H, 6.17; N, 7.09%.

4.23. Bis[4-(N-methyl-N-phenylamino)phenyl]-phenylphosphine oxide (**5b**)

The procedure was similar to that for **5a**; **5b** was obtained as colorless oil in 71% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 3.32 (s, 6H), 6.81 (dd, ^3J(H, H) = 8.8 Hz, ^4J(P, H) = 2.1 Hz, 4H), 7.11–7.68 (m, 19 H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 40.1, 125.0, 125.5, 128.2 (d, ^3J(C, P) = 11.9 Hz), 129.7, 131.1, 132.1 (d, ^2J(C, P) = 9.5 Hz), 133.3 (d, ^2J(C, P) = 11.1 Hz), 134.2 (d, ^1J(C, P) = 103.2 Hz), 147.6, 151.5; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 30.8 (s); MS (EI), *m/z* (%): 488 (M^+, 62), 489 (19), 487 (57), 411 (8); Anal. Calc. for $C_{32}H_{29}N_2OP$: C, 78.67; H, 5.98; N 5.73. Found: C, 78.41; H, 6.21; N, 5.89%.

4.24. [4-(N-Methyl-N-phenylamino)phenyl]-diphenylphosphine oxide (**5c**)

The procedure was similar to that for **5a**; **5c** was obtained as colorless oil in 79% yield. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.33 (s, 3H), 6.84 (dd, ^3J(H, H) = 8.8 Hz, ^4J(P, H) = 2.1 Hz, 2H), 7.19–7.68 (m, 17H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 40.4, 114.7 (d, ^3J(C, P) = 13.6 Hz), 125.7, 126.2, 128.7 (d, ^3J(C, P) = 11.9 Hz), 130.2, 131.9, 132.5 (d, ^2J(C, P) = 9.5 Hz), 132.8 (d, ^1J(C, P) = 109.0 Hz), 133.7 (d, ^2J(C, P) = 11.1 Hz), 133.9 (d, ^1J(C, P) = 103.1 Hz), 147.9, 152.1; ^{31}P-NMR (101 MHz, $CDCl_3$); δ 30.4 (s); MS (EI), *m/z* (%): 383 (M^+, 71), 384 (19), 382 (100), 306 (10); Anal. Calc. for $C_{25}H_{22}NOP$: C, 78.31; H, 5.78; N, 3.65. Found: C, 78.14; H, 5.91; N, 3.83%.

4.25. Tris(4-carbomethoxyphenyl)phosphine oxide (**6a**) [17b,25a,29b,d]

A mixture of **1a** (515 mg, 1.0 mmol), $PdCl_2$ (13 mg, 0.075 mmol), PPh_3 (40 mg, 0.15 mmol), triethylamine (456 mg, 4.5 mmol), methanol (10 ml) and DMF (10 ml) was stirred overnight at 125 °C in an autoclave under 75 bar CO. After cooling to room temperature the CO was carefully released in a fume cupboard, and the mixture was diluted with water 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 product was purified by flash chromatography (EtOAc/hexane = 8/1); **6a** was obtained as white crystalline solid (431 mg, 95%). ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 3.95 (s, 9H), 7.76 (dd, ^3J(P, H) = 11.7 Hz, ^3J(H, H) = 8.4 Hz, 6H), 8.14 (dd, ^4J(P, H) = 2.4 Hz, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 52.9, 130.1 (d, ^3J(C, P) = 11.9 Hz), 132.4 (d, ^2J(C, P) = 10.3 Hz), 134.2, 136.6 (d, ^1J(C, P) = 100.8 Hz), 166.4; ^{31}P-NMR (101 MHz, $CDCl_3$): δ 28.1 (s); MS (EI), *m/z* (%): 452 (M^+, 65), 451 (100). Anal. Calc. for $C_{24}H_{21}O_7P$: C, 63.72; H, 4.68. Found: C, 63.65; H, 4.74%.

4.26. Bis(4-carbomethoxyphenyl)phenylphosphine oxide (**6b**) [17b,29a,c]

The procedure was similar to that for **6a**; **6b** was obtained as white crystalline solid in 92% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 3.94 (s, 6H), 7.47–7.68 (m, 5H), 7.76 (dd, ^3J(P, H) = 11.9 Hz, ^3J(H, H) = 8.4 Hz, 4H), 8.12 (dd, ^4J(P, H) = 2.5 Hz, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 52.8, 129.2 (d, ^3J(C, P) = 12.7 Hz), 129.9 (d, ^3J(C, P) = 12.7 Hz), 131.2, 132.2 (d, ^2J(C, P) = 9.5 Hz), 132.3, 132.5 (d, ^2J(C, P) = 10.3 Hz), 133.4 (d, ^1J(C, P) = 104.0 Hz), 137.4 (d, ^1J(C, P) = 100.8 Hz), 166.5; ^{31}P-NMR (101 MHz, $CDCl_3$) δ 28.2; MS (EI), *m/z* (%): 394 (M^+, 52), 393 (100), 395 (11), 396 (2); Anal. Calc. for $C_{22}H_{19}O_5P$: C, 67.00; H, 4.86. Found: C, 66.92; H, 4.86%.

4.27. (4-Carbomethoxyphenyl)diphenylphosphine oxide (**6c**) [6f,8a,17b,29e]

The procedure was similar to that for **6a**; **6c** was obtained as white crystalline solid in 92% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, Me_4Si): δ 3.93 (s, 3H), 7.46–7.60 (m, 6H), 7.64–7.69 (m, 4H), 7.77 (dd, ^3J(H, H) = 8.4 Hz, ^3J(P, H) = 11.4 Hz, 2H), 8.12 (dd, ^4J(H, H) = 2.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 52.5, 128.5, 128.7 (d, ^3J(C, P) = 12.7 Hz), 129.5 (d, ^3J(C, P) = 11.9 Hz), 131.8 (d, ^1J(C, P) = 104.0 Hz), 132.1 (d, ^2J(C, P) = 10.3 Hz), 132.3 (d, ^2J(C, P) = 9.5 Hz), 133.3, 137.5 (d, ^1J(C, P) = 100.0 Hz), 166.2; ^{31}P-NMR (101 MHz, $CDCl_3$) δ 28.9; MS (EI), *m/z* (%): 336 (M^+, 82), 335 (100); HRMS (EI, *m/z*) Calc. for $C_{20}H_{18}O_3P$ (M^+ + 1): 337.09933. Found: 337.09965; Anal. Calc. for $C_{20}H_{17}O_3P$: C, 71.40; H, 5.13. Found: C, 71.24; H, 5.18%.

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