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Palladium-catalyzed air-based oxidative coupling of arylboronic acids with H-phosphine oxides leading to aryl phosphine oxides†

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We present a novel and highly efficient methodology that allows for the construction of C–P bonds *via* the palladium-catalyzed air-based oxidative coupling of various commercially available arylboronic acids with easily oxidized H-phosphine oxides leading to valuable aryl phosphine oxides, particularly triarylphosphine oxides, with the use of air as the green oxidant, broad substrate applicability and good to excellent yields. The described catalytic system should be an efficient complement to the Chan–Lam type reaction and be useful in synthetic programs.

Introduction

Owing to their great importance and broad applications in medicinal chemistry,[1] materials science,[2] organic synthesis[3] and ligand chemistry,[4] aryl phosphine oxides, especially triarylphosphine oxides, have attracted increasing attention in the past two decades, and the number of synthetic pathways to these compounds has increased remarkably over the years. Apart from their traditional preparation from readily hydrolyzable $Ph_2P(O)Cl$ and organometallic reagents, which suffers from a lack of functionality tolerance, transition-metal-catalyzed direct P-arylation of aromatic substrates has emerged as a very appealing strategy for the synthesis of valuable aryl phosphine oxides. Since the pioneering work on palladium-catalyzed cross-coupling of aryl halides with dialkyl phosphites was reported by the Hirao group,[5] researchers have developed the palladium-,[6] nickel-,[7] copper-[8] and manganese-catalyzed[9] phosphination of various aryl partners with phosphorus-based nucleophiles to synthesize aryl phosphine oxides over the years. However, most of these methods suffer from poor substrate scopes, the need for extra additives, unsatisfactory yields or drastic conditions not compatible with substrates containing sensitive functional groups, and there is still a strong need for developing more convenient and efficient approaches to the preparation of aryl phosphine oxides.

The last two decades have witnessed the rapid development of boron chemistry.[10] Arylboronic acids are nontoxic, easily commercially available and structurally diverse building blocks among various boron compounds. Undoubtedly, owing to these attractive features, arylboronic acids occupy a special place in organic synthesis and catalysis, and are the most extensively versatile reagents in transition-metal-catalyzed C_{sp2}-X bond cross-couplings for the effective formation of C–C,[11] C–N[12] and C–S[13] bonds. Nevertheless, in stark contrast, only a few examples of the C–P bond forming reactions using phenylboronic acids as substrates have been reported. Only recently, the first Pd-catalyzed cross-coupling of arylboronic acids with H-phosphonates has been revealed.[14] Although this example firstly showed that arylboronic acids are potential coupling partners for C–P bond formation, their general use faces severe limitations due to a limited substrate scope unsuitable for H-phosphine oxides as substrates because of the addition of *p*-benzoquinone with them and their oxidation by the reaction system,[15] as well as the need for microwave heating, environmentally-unbenign *p*-benzoquinone as the oxidant, and DMF with a high boiling point as the solvent, which are neither economically attractive nor environmentally benign. Furthermore, our group reported the Cu-catalyzed C–P bond formation *via* a Chan–Lam type reaction using arylboronic acids under mild conditions,[16] but the method also suffered heavily from poor substrate scope, only affording a trace of triarylphosphine oxides using H-phosphine oxides as substrates owing to their oxidation by the catalytic system. Very recently, there have been significant advances in this field of research. Our group reported the first Ni-catalyzed C–P

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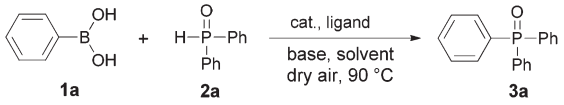
cross-coupling of arylboronic acids with P(O)H compounds.[17] Although this method provides a general tool for the synthesis of various valuable triarylphosphine oxides in good to excellent yields, the protocol did not tolerate well some functionalities such as aldehyde, methylthio, vinyl and pyridyl. Therefore, developing a mild and efficient method with a broader substrate scope to access valuable triarylphosphine oxides *via* the transition-metal-catalyzed cross-coupling of arylboronic acids with H-phosphine oxides is still desirable. Herein we reported a novel and highly efficient methodology for the preparation of aryl phosphine oxides, particularly triarylphosphine oxides, through the Pd-catalyzed air-based oxidative coupling of a wide range of commercially available arylboronic acids with various H-phosphine oxides. This reaction was accidently found during work on optimizing our Ni-catalyzed phosphinylation of arylboronic acids,[17] which also remarkably gave triarylphosphine oxides using Pd-catalysts instead of Ni-catalysts when oxygen was introduced. This protocol has some notable advantages including using air as the green oxidant, relatively milder conditions, no additional microwave radiation, broader substrate applicability and moderate to excellent yields.

Results and discussion

Initially, under dry air, the coupling between phenylboronic acid (**1a**) and diphenylphosphine oxide (**2a**) as model substrates was carried out to evaluate the catalytic activity of various transition-metal complexes including Pd, Cu and Ni salts. Among these metal salts surveyed, Pd salts, particularly $Pd(OAc)_2$, was found to be the most effective catalyst to generate the desired product **3a** in 93% isolated yield in the presence of $Pd(OAc)_2$ (0.025 mmol), dppb (0.025 mmol), K_2CO_3 (0.25 mmol) at 90 °C for 24 h (Table 1, entry 4). Other Pd salts such as $PdCl_2$, $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$ afforded the desired products in 75%, 87% and 90% yields, respectively (entries 1–3). In contrast, other metal salts such as $Cu(OAc)_2$ and $Ni(OAc)_2$ only produced product **3a** in very low yields under similar reaction conditions (entries 5 and 6). Without catalysts, the coupling did not occur, indicating that the $Pd(OAc)_2$ catalyst is essential to obtain a high yield of **3a**. A screening of ligands revealed that dppb was the best choice (entry 4), and omitting the ligand from the reaction mixture resulted in a lower yield of 35%, demonstrating that the ligand was crucial to the coupling (entry 12). Other ligands and corresponding yields of **3a** were as follows: PPh_3, 84%; dppp, 86%; 1,10-phen, 66% and 2,2-bipyridyl (bpy), 45%. Subsequent survey on the role of bases for this coupling disclosed K_2CO_3 was the most suitable base (entry 4). In addition to K_2CO_3, Na_2CO_3 was also an appropriate choice and gave a 92% yield (entry 13). Other bases such as Cs_2CO_3, K_3PO_4, Et_3N only afforded **3a** in 70–73% yields (entries 14–16). Without the participation of bases, apparent yield reduction was observed (entry 17). Solvents also highly affected this reaction. A survey of solvents including 1,4-dioxane, DMF, toluene, CH_3CN, and 1,2-dichloroethane (DCE) revealed dioxane was the best solvent (entries 4, 18–21). Using pure oxygen as the oxidant did not enhance the reaction yield, also affording **3a** in 91% yield (entry 22). Notably, under an argon atmosphere, the coupling only afforded the desired product in 20% yield, illustrating that oxygen was involved in the reaction process (entry 23). Decreasing the reaction temperature to 80 °C led to a slightly lower yield of 85% and raising the temperature to 100 °C did not increase the yield but gave a decrease of the coupling product (65%).

Table 1 Optimization of reaction conditions[a]



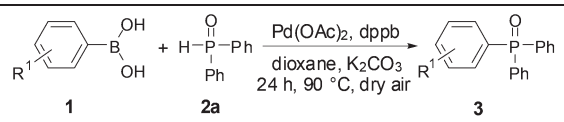
1a **2a** **3a**

Entry	Catalyst	Ligand	Base	Solvent	Yield[b] (%)
1	$PdCl_2$	dppb	K_2CO_3	Dioxane	75
2	$Pd(PPh_3)_2Cl_2$	—	K_2CO_3	Dioxane	87
3	$Pd(PPh_3)_4$	—	K_2CO_3	Dioxane	90
4	**$Pd(OAc)_2$**	**dppb**	**K_2CO_3**	**Dioxane**	**93**
5	$Cu(OAc)_2$	dppb	K_2CO_3	Dioxane	5
6	$Ni(OAc)_2$	dppb	K_2CO_3	Dioxane	19
7	—	dppb	K_2CO_3	Dioxane	0
8	$Pd(OAc)_2$	PPh_3	K_2CO_3	Dioxane	84
9	$Pd(OAc)_2$	dppp	K_2CO_3	Dioxane	86
10	$Pd(OAc)_2$	1,10-Phen	K_2CO_3	Dioxane	66
11	$Pd(OAc)_2$	bpy	K_2CO_3	Dioxane	45
12	$Pd(OAc)_2$	—	K_2CO_3	Dioxane	35
13	$Pd(OAc)_2$	dppb	Na_2CO_3	Dioxane	92
14	$Pd(OAc)_2$	dppb	Cs_2CO_3	Dioxane	73
15	$Pd(OAc)_2$	dppb	K_3PO_4	Dioxane	72
16	$Pd(OAc)_2$	dppb	Et_3N	Dioxane	70
17	$Pd(OAc)_2$	dppb	—	Dioxane	54
18	$Pd(OAc)_2$	dppb	K_2CO_3	DMF	45
19	$Pd(OAc)_2$	dppb	K_2CO_3	Toluene	82
20	$Pd(OAc)_2$	dppb	K_2CO_3	CH_3CN	60
21	$Pd(OAc)_2$	dppb	K_2CO_3	DCE	67
22	$Pd(OAc)_2$	dppb	K_2CO_3	Dioxane	91[c]
23	$Pd(OAc)_2$	dppb	K_2CO_3	Dioxane	20[d]

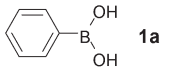
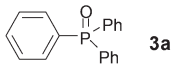
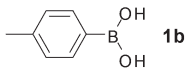
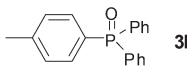
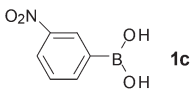
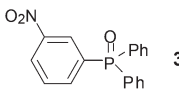
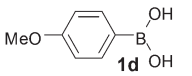
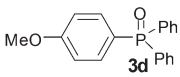
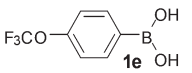
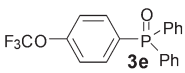
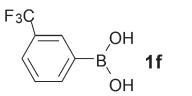
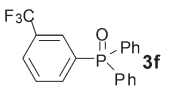
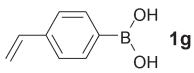
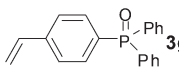
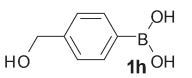
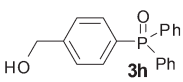
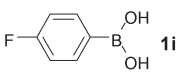
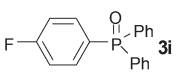
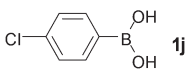
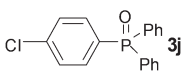
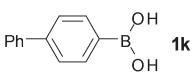
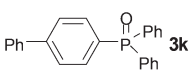
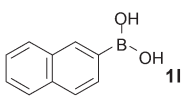
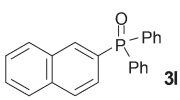
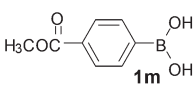
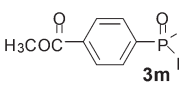
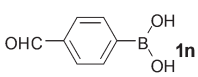
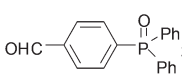
[a] Reaction conditions: **1a** (0.75 mmol), diphenylphosphine oxide (0.5 mmol), catalyst (5 mol%), ligand (5 mol% for bidentate, 10 mol% for monodentate), base (0.25 mmol), solvent (1 mL), under dry air, 90 °C, 24 h. [b] Isolated yield. [c] Under O_2. [d] Under Ar.

Under the best conditions shown in footnote *a*, Table 2, we turned our attention to survey the cross-coupling of a variety of arylboronic acids with diphenylphosphine oxide **2a** to examine the generality of the methodology. As shown in Table 2, various valuable triarylphosphine oxides can be conveniently and efficiently obtained by this novel palladium-catalyzed air-based phosphinylation reaction of arylboronic acids, and the corresponding oxidative coupling products were produced in moderate to excellent yields (**3a–3s**). In general, both electron-rich and electron-deficient arylboronic acids were suitable for this method. Thus, a variety of functionalities, such as methyl (**3b**), nitro (**3c**), alkoxyl (**3d** and **3e**), trifluoromethyl (**3f**), hydroxyl (**3h**), fluoro (**3i**), chloro (**3j**), phenyl (**3k** and **3l**), carboxyl (**3m**), aldehyde (**3n**), cyano (**3o**), aminoacetyl (**3p**), methylthio (**3s**) and amino (**3q**) groups, were all tolerated under the reaction conditions. Notably, arylboronic acids bearing a strong electron-withdrawing group such as nitro and

Table 2 Palladium-catalyzed cross-coupling of arylboronic acids with diphenylphosphine oxide[a]



1 2a 3

Entry	Substrate 1	Product 3	Yield[b] (%)
1			93
2			92
3			74[c]
4			80[d]
5			94
6			88
7			60[c]
8			87
9			79
10			48
11			87
12			93
13			88
14			61

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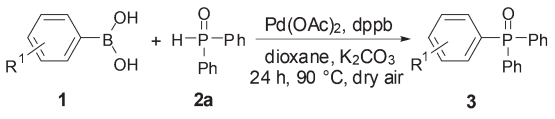
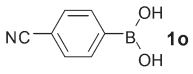
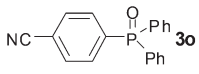
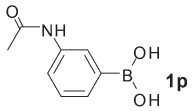
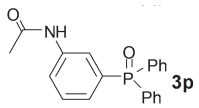
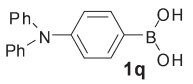
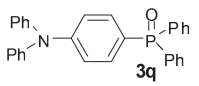
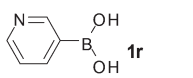
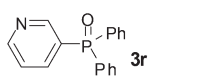
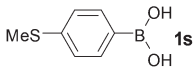
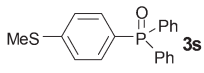


1 2a 3

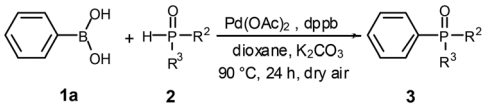
Entry	Substrate 1	Product 3	Yield[b] (%)
15			71[c]
16			95[c]
17			76[d]
18			88
19			90

[a] Reaction conditions: **1a** (0.75 mmol), **2a** (0.5 mmol), $Pd(OAc)_2$ (5 mol%), dppb (5 mol%), K_2CO_3 (0.25 mmol), dioxane (1 mL), under dry air, 90 °C, 24 h. [b] Isolated yield. [c] Using Na_2CO_3 (0.25 mmol). [d] Using Cs_2CO_3 (0.25 mmol).

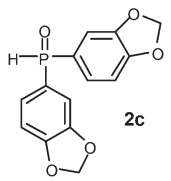
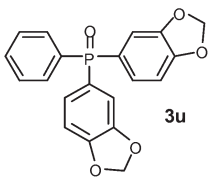
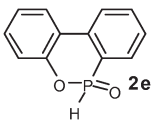
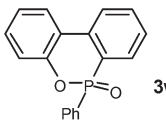
trifluoromethyl groups were good substrates for this oxidative coupling reaction, giving the corresponding products in high yields (entries 3 and 6). Interestingly, (4-vinylphenyl)boronic acid (**1g**) was also compatible with this reaction with high regioselectivity, thus affording the corresponding coupling product **3g** in 60% yield (entry 7). More interestingly, an aldehyde substrate having a reactive aldehyde unit could also be used in the reaction to give the desired triarylphosphine oxide **3n** selectively in a moderate yield without needing any protection of the aldehyde group (entry 14). Moreover, heteroaromatic arylboronic acids such as **1r** could also undergo the coupling smoothly, resulting in a high yield of 88% (entry 18). It was particularly noteworthy that when electron-rich 4-methylthiophenylboronic acid **1s** having a methylthio acting as sulfur poisoning of metal catalysts frequently was used as the substrate, however, to our delight, we did not observe that the sulfur species dramatically deactivated the Pd catalyst and the reaction afforded an excellent yield of 90% (entry 19). Obviously, this protocol with broad substrate applicability afforded a general and practical method for the preparation of valuable triarylphosphine oxides.

To gain more insight into the substrate scope of the reaction, various P(O)H compounds including H-phosphine oxides, H-phosphinates and H-phosphonates as cross-coupling partners were evaluated (Table 3). Gratifyingly, in addition to diphenylphosphine oxide, other H-phosphine oxides such as

Table 3 Palladium-catalyzed cross-coupling of phenylboronic acids with $HPOR^2R^3$ [a]



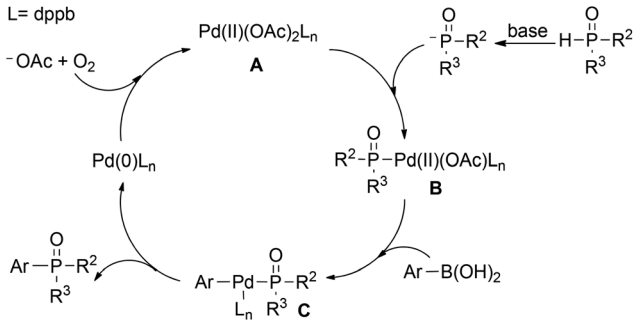
1a 2 3

Entry	Substrate 2	Product 3	Yield[b] (%)
1	 2b	 3t	88
2	 2c	 3u	91
3	 2d	 3v	90[c]
4	 2e	 3w	90[c]
5	 2f	 3x	56

[a] Reaction conditions: phenylboronic acids (0.75 mmol), **2a** (0.5 mmol), $Pd(OAc)_2$ (5 mol%), dppb (5 mol%), K_2CO_3 (0.25 mmol), dioxane (1 mL), under dry air, 90 °C, 24 h. [b] Isolated yield. [c] Using Na_2CO_3 (0.25 mmol).

2b and **2c** all exhibited good compatibility as well. Thus, the corresponding products **3t** and **3u** were obtained in 88% and 91% yields, respectively (entries 1 and 2). In addition, H-phosphinates such as hydrogen ethyl phenylphosphinate **2d** and 6*H*-dibenz[*c*,*e*][1,2]oxaphosphorin-6-oxide **2e** could also be transformed to the corresponding P-arylated products in high yields using Na_2CO_3 as the base. However, diethyl phosphonate **2f** as the substrate only gave a lower yield of 56% under similar reaction conditions, indicating that the yields depended primarily upon the electronic properties of P(O)H compounds.

A possible mechanism for the coupling of arylboronic acids with $HP(O)R^2R^3$ is outlined in Scheme 1. Firstly, the Pd(II) complex **A** reacted with the phosphorous nucleophile generated by deprotonation of the P(O)H compound with the assistance of a base to provide intermediate **B**.[14] Following association with arylboronic acids would give **C**, which afforded the desired coupling product and Pd(0) species by subsequent reductive elimination.[14,18] Finally, the Pd(0) species was oxidized by O_2 from air, leading to the regeneration of Pd(II) complex **A** as a catalytically active species.



Scheme 1 The possible mechanism for the palladium-catalyzed air-based oxidative coupling reaction.

Conclusions

In conclusion, we have successfully developed a novel and highly efficient methodology that allows for the construction of C–P bonds *via* the oxidative coupling of a wide range of readily available arylboronic acids with various H-phosphine oxides under mild reaction conditions in the presence of a palladium catalyst and dry air, providing a practical and powerful synthetic tool for the preparation of various aryl phosphine oxides, particularly valuable triarylphosphine oxides. Importantly, the noticeable advantages of this protocol include using air as the green oxidant, no need of microwave radiation, the remarkable functional group tolerance and good to excellent yields. The described catalytic system should be an efficient complement to the Chan–Lam type reaction and a great improvement to the known palladium-catalyzed method and would find broad applications in modern synthetic chemistry due to these advantages.

Experimental

All reactions were carried out under a dry air atmosphere. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. The solvent 1,4-dioxane was refluxed over sodium and distilled under argon before use. ^{31}P, ^{1}H and ^{13}C NMR were performed in $CDCl_3$ or in $(CD_3)_2SO$, using tetramethylsilane (TMS) as the internal standard and 85% H_3PO_4 as the external standard for ^{31}P NMR. New compounds were further characterized by HRMS-ESI-ion trap.

General procedure for the synthesis of 3a–3x

$Pd(OAc)_2$ (5 mol%), dppb (5 mol%), K_2CO_3 or indicated base (0.25 mmol), arylboronic acids (0.75 mmol), P(O)H (0.5 mmol) were dissolved in freshly distilled 1,4-dioxane (1 mL) under excess dry air (200 mL) at room temperature and stirred at 90 °C for 24 h. The resulting crude product was purified by flash chromatography using a mixture of petroleum ether and ethyl acetate as the eluent to give the desired product.

Triphenylphosphine oxide (3a).[17] (CAS number: 791-28-6). White solid; m.p.: 154.5–156.2 °C; 129 mg, 93%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.61 (m, 6 H), 7.51–7.48 (m, 3 H), 7.43–7.39 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.5 (d, J = 102.6 Hz), 132.1 (d, J = 9.8 Hz), 131.9 (d, J = 2.6 Hz), 128.5 (d, J = 12.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.10. MS-ESI: m/z 279.1 $[M + H]^+$.

Diphenyl(*p*-tolyl)phosphine oxide (3b).[17] (CAS number: 6840-28-4). White solid; m.p.: 129.5–130.2 °C; 134 mg, 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.62 (m, 4 H), 7.56–7.48 (m, 4 H), 7.44–7.40 (m, 4 H), 7.26–7.23 (m, 2 H), 2.37 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5 (d, J = 2.6 Hz), 132.9 (d, J = 104.1 Hz), 132.2 (d, J = 10.2 Hz), 132.1 (d, J = 10.0 Hz), 131.9 (d, J = 2.8 Hz), 129.3 (d, J = 12.5 Hz), 129.2 (d, J = 106.4 Hz), 128.5 (d, J = 11.9 Hz), 21.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.13. MS-ESI: m/z 293.2 $[M + H]^+$. Anal. Calcd for $C_{19}H_{17}OP$: C, 78.07; H, 5.86. Found: C, 78.13; H, 5.64.

(3-Nitrophenyl)diphenylphosphine oxide (3c).[8f] (CAS number: 31638-87-6). Yellow oil; 119 mg, 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48–8.44 (dt, 1 H), 8.38–8.34 (m, 1 H), 8.07–8.02 (m, 1 H), 7.69–7.63 (m, 5 H), 7.60–7.56 (m, 2 H), 7.51–7.46 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2 (d, J = 13.8 Hz), 137.8 (d, J = 9.4 Hz), 135.9 (d, J = 100.8 Hz), 132.7 (d, J = 2.5 Hz), 132.1 (d, J = 10.0 Hz), 131.2 (d, J = 106.0 Hz), 130.0 (d, J = 12.0 Hz), 129.0 (d, J = 12.4 Hz), 126.8 (d, J = 11.8 Hz), 126.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.40. MS-ESI: m/z 362.1 $[M + K]^+$.

(4-Methoxyphenyl)diphenylphosphine oxide (3d).[17] (CAS number: 795-44-8). White solid; m.p.: 114.2–115.1 °C; 123 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.61 (m, 4 H), 7.59–7.53 (m, 2 H), 7.52–7.47 (m, 2 H), 7.44–7.39 (m, 4 H), 6.96–6.91 (m, 2H), 3.80 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, J = 2.7 Hz), 134.0 (d, J = 11.0 Hz), 133.0 (d, J = 104.7 Hz), 132.1 (d, J = 9.7 Hz), 131.8 (d, J = 2.1 Hz), 128.5 (d, J = 12.1 Hz), 123.6 (d, J = 110.5 Hz), 114.1 (d, J = 13.2 Hz), 55.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.09. MS-ESI: m/z 309.1 $[M + H]^+$. Anal. Calcd for $C_{19}H_{17}O_2P$: C, 74.02; H, 5.56. Found: C, 73.62; H, 5.21.

Diphenyl(4-(trifluoromethoxy)phenyl)phosphine oxide (3e).[17] (CAS number: 1448632-02-7). Colorless oil; 170 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.62 (m, 6 H), 7.57–7.52 (m, 2 H), 7.48–7.44 (m, 4 H), 7.29–7.26 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0 (dq, J = 1.65 Hz), 134.1 (d, J = 11.0 Hz), 132.3 (d, J = 2.7 Hz), 132.1 (d, J = 10.1 Hz), 132.0 (d, J = 105.2 Hz), 131.4 (d, J = 104.3 Hz), 128.7 (d, J = 12.3 Hz), 120.6 (d, J = 13.0 Hz), 120.4 (q, J = 258.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.13. MS-ESI: m/z 363.1 $[M + H]^+$.

Diphenyl(3-(trifluoromethyl)phenyl)phosphine oxide (3f).[17] (CAS number: 62754-67-0). Colorless oil; 152 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 11.9 Hz, 1 H), 7.85–7.78 (m, 2 H), 7.68–7.62 (m, 4 H), 7.61–7.55 (m, 3 H), 7.50–7.46 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4 (d, J = 9.4 Hz), 134.5 (d, J = 101.6 Hz), 132.5, 132.1 (d, J = 10.2 Hz), 131.8 (d, J = 104.7 Hz), 131.3 (dq, J = 13.5, 31.6 Hz), 129.2 (d, J = 11.7 Hz), 128.8 (d, J = 12.2 Hz), 123.7 (q, J = 274.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.09. MS-ESI: m/z 347.1 $[M + H]^+$.

(4-Ethenylphenyl)diphenylphosphine oxide (3g).[19] (CAS number: 47182-95-6). Colorless oil; 91 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68–7.59 (m, 6 H), 7.55–7.50 (m, 2 H), 7.48–7.42 (m, 6 H), 6.72 (dd, J = 17.6, 10.9 Hz, 1 H), 5.83 (d, J = 17.6 Hz, 1 H), 5.35 (d, J = 10.9 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1 (d, J = 2.9 Hz), 136.0, 132.7 (d, J = 103.8 Hz), 132.5 (d, J = 10.1 Hz), 132.1 (d, J = 9.8 Hz), 132.0 (d, J = 2.4 Hz), 131.7 (d, J = 104.2 Hz), 128.6 (d, J = 12.2 Hz), 126.3 (d, J = 12.5 Hz), 116.6. ^{31}P NMR (162 MHz, CDCl3): δ 28.95. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.95. MS-ESI: m/z 305.1 $[M + H]^+$.

(4-(Hydroxymethyl)phenyl)diphenylphosphine oxide (3h) (CAS number: 5068-20-2). White solid; m.p.: 179.2–181.3 °C; 134 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.55 (m, 4 H), 7.53–7.38 (m, 8 H), 7.36–7.33 (m, 2 H), 4.68 (m, 2 H), 4.36 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 132.3 (d, J = 104.2 Hz), 132.2, 132.1 (d, J = 10.1 Hz), 132.0, 130.4 (d, J = 109.1 Hz), 128.6 (d, J = 12.3 Hz), 126.7 (d, J = 12.7 Hz), 64.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.13. MS-ESI: m/z 309.1 $[M + H]^+$.

(4-Fluorophenyl)diphenylphosphine oxide (3i).[17] (CAS number: 18437-73-5). White solid; m.p.: 133.6–135.5 °C; 117 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$): 7.69–7.61 (m, 6 H), 7.56–7.51 (m, 2 H), 7.47–7.42 (m, 4 H), 7.16–7.10 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1 (dd, J = 253.4, 3.3 Hz), 134.6 (dd, J = 11.1, 8.9 Hz), 132.4 (d, J = 104.6 Hz), 132.1 (d, J = 3.4 Hz), 132.0 (d, J = 10.1 Hz), 128.7 (dd, J = 106.3, 3.4 Hz), 128.6 (d, J = 12.3 Hz), 116.0 (dd, J = 22.1, 13.1 Hz). ^{31}P NMR (162 MHz, CDCl3): δ 28.38. MS-ESI: m/z 297.1 $[M + H]^+$. Anal. Calcd for $C_{18}H_{14}FOP$: C, 72.97, H, 4.76. Found: C, 72.53; H, 4.52.

(4-Chlorophenyl)diphenylphosphine oxide (3j).[17] (CAS number: 34303-18-9). White solid; m.p.: 143.7–145.2 °C; 75 mg, 48%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67–7.52 (m, 8 H), 7.48–7.41 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7 (d, J = 3.4 Hz), 133.6 (d, J = 10.8 Hz), 132.3 (d, J = 2.4 Hz), 132.2 (d, J = 105.1 Hz), 132.1 (d, J = 10.0 Hz), 131.3 (d, J = 104.3 Hz), 129.0 (d, J = 12.7 Hz), 128.7 (d, J = 12.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.46. MS-ESI: m/z 313.1 $[M + H]^+$.

(4-Biphenylyl)diphenylphosphine oxide (3k).[17] (CAS number: 1942-83-2). White solid; m.p.: 156.1–157.2 °C; 154 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76–7.66 (m, 8 H), 7.61–7.54 (m, 4 H), 7.50–7.43 (m, 6 H), 7.40–7.36 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8 (d, J = 2.7 Hz), 140.0, 133.2, 132.7 (d, J = 10.8 Hz), 132.3, 132.1, 132.0 (d, J = 2.5 Hz), 131.2 (d, J = 105.4 Hz), 129.1, 128.6 (d, J = 12.3 Hz), 127.7 (d, J = 105.4 Hz), 127.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.09. MS-ESI: m/z 355.2 $[M + H]^+$.

2-Naphthyldiphenylphosphine oxide (3l).[17] (CAS number: 28402-08-6). Light yellow oil; 152 mg, 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J = 14.0 Hz, 1 H), 7.90–7.84 (m, 3 H), 7.74–7.69 (m, 4 H), 7.66–7.61 (m, 1 H), 7.59–7.50 (m, 4 H), 7.47–7.43 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ134.7 (d, J = 2.3 Hz), 134.1 (d, J = 9.4 Hz), 132.5 (d, J = 104.6 Hz), 132.3 (d, J = 13.2 Hz), 132.1 (d, J = 10.0 Hz), 132.0 (d, J = 2.7 Hz), 129.7 (d, J = 103.9 Hz), 129.0, 128.6 (d, J = 12.5 Hz), 128.4, 128.3, 127.4, 127.1, 126.9 (d, J = 10.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.08. MS-ESI: m/z 329.2 $[M + H]^+$.

(*p*-Carbomethoxyphenyl)diphenylphosphine oxide (3m).[17] (CAS number: 5032-55-3). White solid; m.p.: 113.4–114.5 °C; 148 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–8.01 (m, 2 H), 7.77–7.72 (m, 2 H), 7.66–7.61 (m, 4 H), 7.56–7.51 (m, 2 H), 7.47–7.42 (m, 4 H), 3.90 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 137.7 (d, J = 100.4 Hz), 133.2 (d, J = 2.7 Hz), 132.3 (d, J = 2.4 Hz), 132.2, 132.1 (d, J = 10.2 Hz), 131.9 (d, J = 104.8 Hz), 129.5 (d, J = 12.2 Hz), 128.7 (d, J = 12.2 Hz), 52.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.50. MS-ESI: m/z 359.1 $[M + Na]^+$. Anal. Calcd for $C_{20}H_{17}O_3P$: C, 71.42; H, 5.09; Found: C, 71.02; H, 5.13.

(*p*-Formylphenyl)diphenylphosphine oxide (3n) (CAS number: 5068-23-5). Colorless oil; 93 mg, 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.07 (s, 1 H), 7.96–7.94 (m, 2 H), 7.87–7.82 (m, 2 H), 7.68–7.63 (m, 4 H), 7.58–7.55 (t, J = 7.4 Hz, 2 H), 7.49–7.46 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7, 139.5 (d, J = 99.4 Hz), 138.5 (d, J = 2.6 Hz), 132.8 (d, J = 10.1 Hz), 132.4 (d, J = 2.4 Hz), 132.1 (d, J = 10.0 Hz), 131.7 (d, J = 105.1 Hz), 129.4 (d, J = 12.1 Hz), 128.8 (d, J = 12.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.32. MS-ESI: m/z 307.1 $[M + H]^+$.

(*p*-Cyanophenyl)diphenylphosphine oxide (3o).[7d] (CAS number: 5032-54-2). Colorless oil; 107 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.71 (m, 4 H), 7.65–7.54 (m, 6 H), 7.49–7.45 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5 (d, J = 98.7 Hz), 132.6 (d, J = 10.3 Hz), 132.5 (d, J = 4.1 Hz), 132.0 (d, J = 10.1 Hz), 131.1 (d, J = 105.3 Hz), 128.9 (d, J = 12.3 Hz), 128.5 (d, J = 12.2 Hz), 117.9, 115.7 (d, J = 4.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.72. MS-ESI: m/z 304.1 $[M + H]^+$. Anal. Calcd for $C_{19}H_{14}NOP$: C, 75.24; H, 4.65; N, 4.62. Found: C, 75.01; H, 4.58; N, 4.34.

(3-Acetaminophenyl)diphenylphosphine oxide (3p) (new compound). White solid; m.p.: 231–232 °C; 159 mg, 95%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.19 (s, 1 H), 7.96–7.90 (m, 2 H), 7.68–7.63 (m, 6 H), 7.61–7.56 (m, 4 H), 7.52–7.47 (m, 1 H), 7.29–7.24 (m, 1 H), 2.06 (s, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.5, 140.5 (d, J = 15.0 Hz), 134.1 (d, J = 102.2 Hz), 133.6 (d, J = 102.2 Hz), 132.9 (d, J = 2.2 Hz), 132.3 (d, J = 9.6 Hz), 130.1 (d, J = 13.2 Hz), 129.6 (d, J = 11.8 Hz), 126.7 (d, J = 9.5 Hz), 123.1, 122.5 (d, J = 11.8 Hz), 24.9. ^{31}P NMR (162 MHz, DMSO-d_6): δ 25.72. IR (film) ν_{max}: 3123, 3051, 2924, 1690, 1591, 1552, 1436, 1310, 1177, 1121, 968, 693, 548 cm^{-1}. HRMS (ESI-ion trap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{18}NO_2PNa$ 358.0973; Found 358.0972. Anal. Calcd for $C_{20}H_{18}NO_2P$: C, 71.63; H, 5.41; N, 4.18. Found: C, 71.33; H, 5.34; N, 3.82.

(4-(Diphenylylamino)phenyl)diphenylphosphine oxide (3q).[20] (CAS number: 887651-41-4). White solid; m.p.: 41.9–43.2 °C; 169 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.67 (m, 4 H), 7.52–7.39 (m, 8 H), 7.30–7.00 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2 (d, J = 2.5 Hz), 146.6, 133.3 (d, J = 10.9 Hz), 133.1 (d, J = 104.3 Hz), 132.1 (d, J = 10.0 Hz), 131.8 (d, J = 2.2 Hz), 129.6, 128.5 (d, J = 12.1 Hz), 125.9, 124.5, 123.2 (d, J = 111.0 Hz), 120.2 (d, J = 12.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.13. MS-ESI: m/z 446.1 $[M + H]^+$.

Diphenyl(3-pyridyl) phosphine oxide (3r).[7d] (CAS number: 678140-94-8). White solid; m.p.: 124.1–125.6 °C; 123 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74–8.71 (m, 2 H), 8.03–7.97 (m, 1 H), 7.66–7.60 (m, 4 H), 7.55–7.51 (m, 2 H), 7.46–7.42 (m, 4 H), 7.38–7.35 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 152.5 (d, J = 12.6 Hz), 139.7 (d, J = 7.7 Hz), 132.4 (d, J = 2.3 Hz), 131.9 (d, J = 10.2 Hz), 131.6 (d, J = 103.6 Hz), 129.1 (d, J = 101.3 Hz), 128.8 (d, J = 12.4 Hz), 123.5 (d, J = 8.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.47. MS-ESI: m/z 280.1 $[M + H]^+$. Anal. Calcd for $C_{17}H_{14}NOP$: C, 73.11; H, 5.05; N, 5.02. Found: C, 72.73; H, 5.07; N, 4.76.

(4-(Methylthio)phenyl)diphenylphosphine oxide (3s).[17] (CAS number: 1466436-16-7). Colorless oil; 146 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.61 (m, 4 H), 7.55–7.48 (m, 4 H), 7.44–7.40 (m, 4 H), 7.25 (dd, J = 8.2, 2.0 Hz, 2 H), 2.45 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4 (d, J = 3.0 Hz), 132.7 (d, J = 104.5 Hz), 132.4 (d, J = 10.5 Hz), 132.1 (d, J = 9.9 Hz), 131.9 (d, J = 2.7 Hz), 128.5 (d, J = 12.1 Hz), 128.1 (d, J = 107.4 Hz), 125.3 (d, J = 12.6 Hz), 14.8. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.88. MS-ESI: m/z 325.1 $[M + H]^+$. Anal. Calcd for $C_{19}H_{17}OPS$: C, 70.35; H, 5.28. Found: C, 70.39; H, 5.45.

Ethyldiphenylphosphine oxide (3t).[17] (CAS number: 1733-57-9). White solid; m.p.: 119.5–121.2 °C; 101 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–7.68 (m, 4 H), 7.52–7.41 (m, 6 H), 2.30–2.21 (m, 2 H), 1.17 (dt, J = 17.4, 7.7 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.8 (d, J = 96.5 Hz), 131.7 (d, J = 2.4 Hz), 130.9 (d, J = 9.2 Hz), 128.7 (d, J = 11.5 Hz), 22.7 (d, J = 73.4 Hz), 5.6 (d, J = 5.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.38. MS-ESI: m/z 231.1 $[M + H]^+$.

Bis(benzo[*d*][1,3]dioxol-5-yl)(phenyl)phosphine oxide (3u).[8f] (CAS number: 1448632-03-8). Colorless oil; 166 mg, 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.61 (m, 2 H), 7.54–7.49 (m, 1 H), 7.45–7.41 (m, 2 H), 7.18–7.12 (m, 2 H), 7.04 (dd, J = 11.5, 1.4 Hz, 2 H), 6.85 (dd, J = 7.9, 2.4 Hz, 2 H), 5.99 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9 (d, J = 2.8 Hz), 148.0 (d, J = 18.2 Hz), 132.8 (d, J = 105.4 Hz), 132.0 (d, J = 9.8 Hz), 131.9 (d, J = 2.5 Hz), 128.6 (d, J = 12.3 Hz), 127.6 (d, J = 10.9 Hz), 125.8 (d, J = 108.9 Hz), 111.6 (d, J = 12.7 Hz), 108.7 (d, J = 15.2 Hz), 101.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.42. MS-ESI: m/z 367.1 $[M + H]^+$.

Ethyl diphenylphosphinate (3v).[17] (CAS number: 1733-55-7). Colorless oil; 110 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ.7.83–7.78 (m, 4 H), 7.52–7.40 (m, 6 H), 4.13–4.06 (m, 2 H), 1.36 (t, J = 7.1 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.1 (d, J = 2.5 Hz), 131.8 (d, J = 137.0 Hz), 131.7 (d, J = 10.1 Hz), 128.6 (d, J = 13.1 Hz), 61.2 (d, J = 5.9 Hz), 16.5 (d, J = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.31. MS-ESI: m/z 247.1 $[M + H]^+$.

6-Phenyl-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine 6-oxide (3w).[21] (CAS number: 36240-32-1). White solid; m.p.: 174.9–175.8 °C; 131 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03–7.96 (m, 2 H), 7.83–7.78 (m, 2 H), 7.67–7.54 (m, 3 H), 7.47–7.33 (m, 4 H), 7.27–7.22 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3 (d, J = 8.3 Hz), 135.8 (d, J = 5.5 Hz), 133.2, 133.1, 132.2 (d, J = 10.9 Hz), 131.0 (d, J = 12.6 Hz), 130.6, 129.7 (d, J = 143.7 Hz), 128.6 (d, J = 13.8 Hz), 128.4 (d, J = 14.1 Hz), 125.1, 125.0 (d, J = 128.4 Hz), 124.7, 123.7 (d, J = 9.5 Hz), 122.1 (d, J = 11.2 Hz), 120.7 (d, J = 6.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.50.

MS-ESI: *m*/*z* 293.1 $[M + H]^+$. Anal. Calcd for $C_{18}H_{13}O_2P$: C, 73.97; H, 4.48. Found: C, 73.54; H, 4.31.

Diethyl phenylphosphonate (3x).[16] (CAS number: 1754-49-0). Colorless oil; 60 mg, 56%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.76 (m, 2 H), 7.55–7.50 (m, 1 H), 7.46–7.41 (m, 2 H), 4.18–4.01 (m, 4 H), 1.30 (t, J = 7.1 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.4 (d, J = 2.7 Hz), 131.8 (d, J = 9.9 Hz), 128.6 (d, J = 14.5 Hz), 128.5 (d, J = 188.2 Hz), 62.2 (d, J = 5.4 Hz), 16.4 (d, J = 6.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 18.79. MS-ESI: *m*/*z* 215.1 $[M + H]^+$.

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