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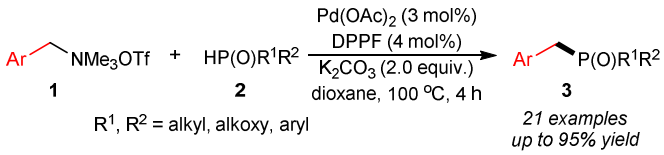

Palladium-catalyzed phosphorylation of benzyl ammonium triflates with P(O)H compounds

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Abstract:

A palladium-catalyzed phosphorylation of benzyl ammonium triflates with P(O)H compounds has been developed. Various benzylphosphorus compounds were produced in good to excellent yields with high functional group tolerance. All the three kinds of hydrogen phosphoryl compounds, i.e. H-phosphonates, H-phosphinates and secondary phosphine oxides, were applicable to this reaction. The succesful scale-up experiment and one-pot synthetic operation also well demonstrated its practicality.

Keywords: Palladium catalysis; Benzyl ammonium triflates; Phosphorylation; Benzylphosphorus compounds.

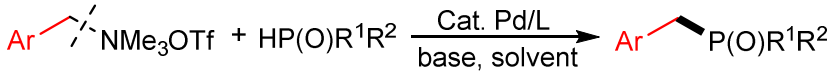
Introduction

Benzylphosphorus compounds are a kind of important synthetic intermediates, for example, for synthesis of alkenes [1]. They also found wide application in medicinal chemistry and material chemistry [2]. Traditional methods for their preparation relied on nucleophilic substitutions of P(O)X compounds with benzyl metals (Li or Mg) and Michaelis-Arbuzov reactions of benzyl halides with phosphites [3], suffering from harsh conditions, poor functional group tolerance, and high toxicity of reagents. In 1980s, Hirao developed a mild Pd-catalyzed cross coupling between aryl halides and P(O)H compounds, which has become a powerful method for constructing C-P bonds [4]. This strategy was also applicable to produce benzyl phosphorus compounds using benzyl halides [5]. Recently, new methods using more available and abundant compounds such as benzyl nitriles, benzyl alcohols and benzyl esters etc. instead of benzyl halides to couple with P(O)H compounds have also been developed [6-9].

Benzyl ammonium triflates are readily accessible amine derivatives. In the last decades, they acted as an excellent benzyl source and were applied in a series of C-C and C-heteroatom (C-B, C-S) bonds forming reactions [10,11]. Recently, Wang reported an Ni-catalyzed cross coupling of aryl, benzyl, and allylammonium salts with P(O)H compounds [12]. It is a very good method for the phosphorylation of aryl and allyl ammonium salts. However, it seems not efficient enough for the synthesis of benzyl phosphorus compounds, especially for the non-π-extended ones. The yields usually were less than 60%. Probably due to the strong ability of oxidative addition of nickel, substrate bearing C_{Ar}-Cl bonds gave a low yield (21% yield). In addition, only

$Ph_2P(O)H$ was demonstrated in the phosphorylation of benzyl ammonium salts. Herein, we report a Pd-catalyzed version with a good complementary reactivity, providing an efficient access to benzyl phosphorus compounds (Scheme 1).

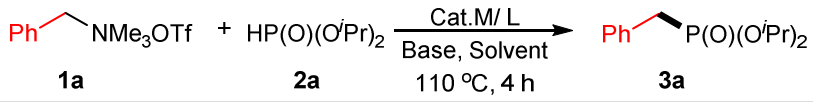
Scheme 1 Pd-catalyzed phosphorylation of benzyl ammonium triflates



Results and discussion

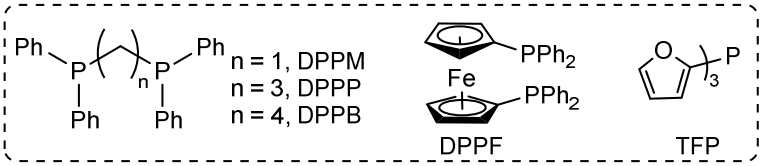
Initially, the reaction of benzyltrimethylammonium triflate (**1a**, 0.2 mmol) and diisopropyl phosphite (**2a**, 1.2 equiv.) was examined in the presence of $Pd(OAc)_2$ (3 mol%), DPPB (4 mol%) and Na_2CO_3 (2.0 equiv.). After heating the mixture at 110 ^oC in dioxane for 4 h, the phosphorylated product **3a** was obtained in 81% GC yield (Table 1, entry 1). Common Pd(II) catalysts such as $PdCl_2$, $Pd(acac)_2$ and $Pd(OTFA)_2$ were tested, however, no better results were observed (Table 1, entries 2-4). Pd(dba)2 could also mediate the reaction, giving **3a** in 54% yield (Table 1, entry 5).[13] It should be noted that no reaction occurred in the absence of palladium catalyst, excluding the possibility that this transformation proceeded through base-promoted nucleophilic substitution (Table 1, entry 6). The phosphine ligand played an important role; no **3a** was detected without addition of phosphine ligands (Table 1, entry 7). Among the monodentate and bisdentate phosphine ligands investigated, DPPF was the best choice, leading to **3a** in 90% yield (Table 1, entries 8-13). A variety of bases were subsequently screened. Cs_2CO_3, K_3PO_4 and K_2CO_3 could also effectively promote this reaction with K_2CO_3 being the best one (Table 1, entries 14-16).

Table 1. Optimization of the reaction conditions.[a]



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

Entry	Cat. [Pd]	Ligand	Base	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	DPPB	Na_2CO_3	dioxane	81
2	$PdCl_2$	DPPB	Na_2CO_3	dioxane	65
3	$Pd(acac)_2$	DPPB	Na_2CO_3	dioxane	73
4	$Pd(OTFA)_2$	DPPB	Na_2CO_3	dioxane	78
5	$Pd(dba)_2$	DPPB	Na_2CO_3	dioxane	54
6	none	DPPB	Na_2CO_3	dioxane	n.d.
7	$Pd(OAc)_2$	none	Na_2CO_3	dioxane	n.d.
8	$Pd(OAc)_2$	DPPM	Na_2CO_3	dioxane	trace
9	$Pd(OAc)_2$	DPPP	Na_2CO_3	dioxane	22
10	$Pd(OAc)_2$	DPPF	Na_2CO_3	dioxane	90
11[c]	$Pd(OAc)_2$	PPh_3	Na_2CO_3	dioxane	64
12[c]	$Pd(OAc)_2$	PPh_2Cy	Na_2CO_3	dioxane	58
13[c]	$Pd(OAc)_2$	TFP	Na_2CO_3	dioxane	trace
14	$Pd(OAc)_2$	DPPF	Cs_2CO_3	dioxane	87
15	$Pd(OAc)_2$	DPPF	K_3PO_4	dioxane	92
16	$Pd(OAc)_2$	DPPF	K_2CO_3	dioxane	95
17	$Pd(OAc)_2$	DPPF	NaO^tBu	dioxane	6
18[d]	$Pd(OAc)_2$	DPPF	K_2CO_3	dioxane	89
19	$Pd(OAc)_2$	DPPF	none	dioxane	n.d.
20	$Pd(OAc)_2$	DPPF	K_2CO_3	THF	88
21	$Pd(OAc)_2$	DPPF	K_2CO_3	toluene	70
22	$Pd(OAc)_2$	DPPF	K_2CO_3	cyclohexane	52
23	$Pd(OAc)_2$	DPPF	K_2CO_3	CH_3CN	87
24	$Pd(OAc)_2$	DPPF	K_2CO_3	DMF	54
25[e]	$Pd(OAc)_2$	DPPF	K_2CO_3	dioxane	95
26[f]	$Pd(OAc)_2$	DPPF	K_2CO_3	dioxane	89



[a] Reaction conditions: **1a** (0.2 mmol), **2a** (1.2 equiv), catalyst (3 mol%), ligand (4 mol%), base (2.0 equiv.), solvent (2.0 mL), N_2, 110 °C, 4 h. [b] GC yield using dodecane as an internal standard. [c] Ligand (8 mol%). [d] K_2CO_3 (1.0 equiv.). [e] 100 °C. [f] 80 °C.

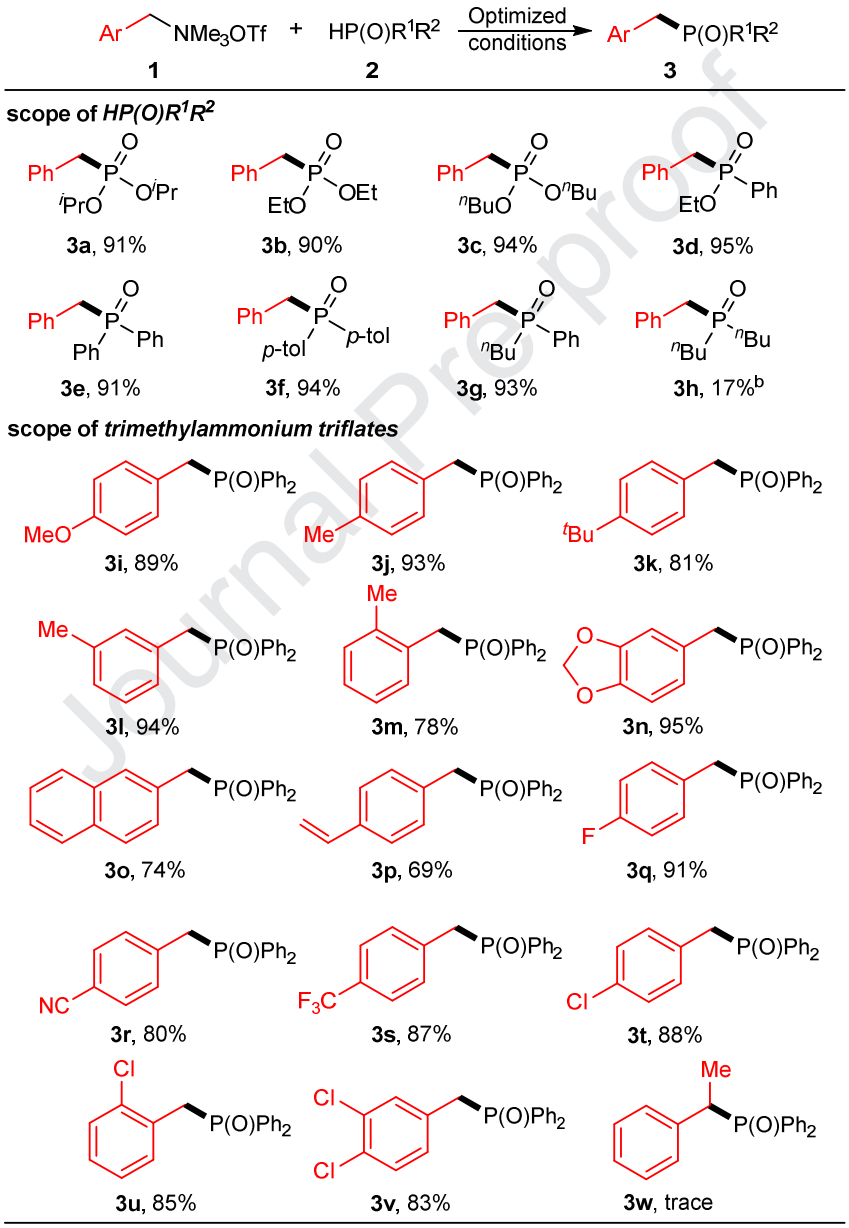
Probably because of the hydrolysing decomposition of H-phosphonate under the strong alkaline conditions, only 6% yield of **3a** was obtained with NaO^{t}Bu (Table 1, entry 17). Reducing the loading of K_2CO_3 to 1.0 equiv led to decrease of the yield; while no **3a** was detected in the absence of any base (Table 1, entries 18 and 19). This C-P bond-forming reaction also took place in other solvents such as THF, toluene, cyclohexane, CH_3CN or DMF, though slightly lower yields of **3a** were given (Table 1, entries 16, 20-24). Final investigation of reaction temperature showed that this reaction could efficiently proceeded at 100 ^{o}C, while further lowering the reaction temperature would reduce the yield of **3a** (Table 1, entries 25 and 26).

With the optimized conditions in hand, substrate scope for both P(O)H compounds and benzyl ammonium triflates was investigated to probe the versatility of this new catalytic reaction (Table 2). In addition to diisopropyl phosphite converted into **3a** in 91% isolated yield, other H-phosphonates like diethyl phosphite and dibutyl phosphite were also applicable to this reaction, producing the corresponding products in 90% and 94% yields, respectively (**3b** and **3c**). H-Phosphinates also proved to be good substrates, exemplified by ethyl phenylphosphinate giving **3d** in 95% yield. Secondary phosphine oxides with aryl groups also showed high reactivity to couple with **1a**, furnishing the expected coupling products in 91-94% yields (**3e-g**). However, when dibutylphosphine oxide was used, low yield of **3h** was obtained under the reaction conditions.

Subsequently, the scope of benzyltrimethylammonium triflates was examined. Substrates bearing electron-donating groups such as OMe, Me, and ^{t}Bu at the benzene

ring coupled readily with $Ph_2P(O)H$, producing the corresponding coupling products in good to high yields (**3i-m**). Condensed nucleus compounds like the oxygen-containing heterocycle **3n** and naphthyl products **3o** could also be obtained in 95 and 74% yields, respectively. Worth noting is that the vinyl group, which is easy

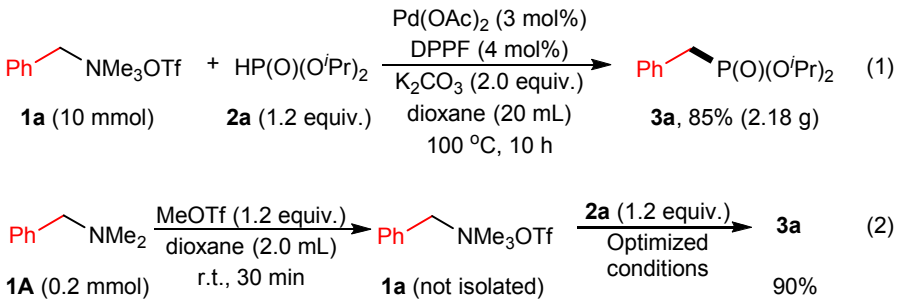
Table 2. Substrate scope.[a]



[a] Reaction conditions: **1** (0.2 mmol), **2** (1.2 equiv), $Pd(OAc)_2$ (3 mol%), DPPF (4 mol%), K_2CO_3 (2.0 equiv.), dioxane (2.0 mL), N_2, 100 °C, 4 h. Isolated yield. [b] GC yield.

to react with P(O)H compounds and polymerize by heating [14], survived well under the reaction conditions, exemplified by **3p** which was obtained in 69% yield. Derivatives bearing electron withdrawing groups such as –F, -CN and $–CF_3$ at the benzene ring presented high reactivity, generating the corresponding organophosphorus products in 80-91% yields (**3q**-**s**). Unlike the reported Ni-catalyzed system, this Pd-catalyzed system had a good compatibility to C_{Ar}–Cl bonds. Both mono- and dichloro substituted benzyl ammonium salts reacted with $Ph_2P(O)H$ regioselectively, giving the C-N bond-phosphorylated products in high yields (**3s-v**, 83-88% yields). However, the more active C_{Ar}–Br bond could not survive under the reaction conditions (not shown). Substrates bearing substituent at the benzyl site were also unworkable, When $PhCH(Me)NMe_3OTf$ was allowed to react with $HP(O)Ph_2$ under the optimized conditions, only a trace amount of desired product **3w** was obtained, the main product was phenylethylene which was generated through β-elimination.

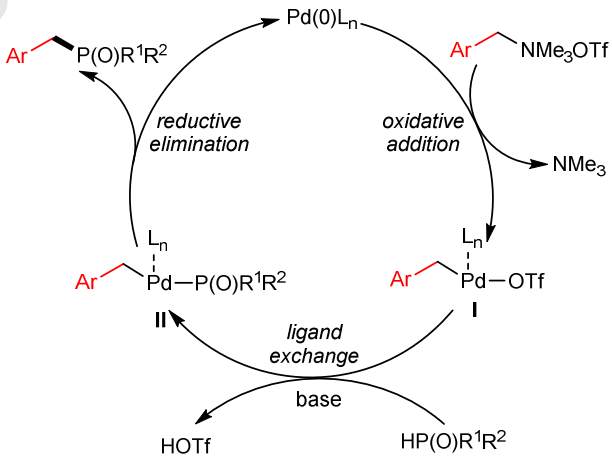
Scheme 2 Scale up and one-pot synthesis.



In order to further explore the potential use of this transformation, a scale-up reaction to 10 mmol scale was performed and an acceptable yield of **3a** (85%, 2.18 g) was obtained (Scheme 2, eq 1). In addition, without isolation of **1a**, the one-pot synthetic operation starting from N,N-dimethylbenzylamine (**1A**) was successfully achieved to produce **3a** in 90% yield, providing a more convenient access for converting organic amines into organophosphorus compounds (Scheme 2, eq 2).

On the basis of previous literatures [10-12, 15], a plausible reaction mechanism was proposed. As shown in Scheme 3, Pd(0) complex firstly added to benzyltrimethylammonium triflates to afford speceis **I** with release of NMe_3. In the presence of a base, **I** subsequently underwent ligand exchange with P(O)H compounds, generating the intermediate **II**. Reductive elimination of **II** produced the target benzyl phosphorus compounds and regenerated the Pd(0) complex to complete the catalytic cycle.

Scheme 3 Plausible reaction mechanism.



Conclusions

In conclusion, we have developed an efficient Pd-catalyzed C-P bond forming reaction through phosphorylation of the readily accessible benzyl ammonium triflates. The reaction allowed all the three kinds of hydrogen phosphoryl compounds to couple with benzyl ammonium salts bearing various functional groups, producing the corresponding benzylphosphorus compounds in good to excellent yields. Gram-scale reaction and one-pot synthetic experiment starting from amines were successfully operated, which not only provide an efficient method for synthesis of benzylphosphorus compounds, but also enriches the application of amines as synthon in organic chemistry.

Acknowledgements

This work is supported by the NSF of Hainan Province (Grant No. 219MS005) and the National NSF of China (Grant Nos. 21871070). Hainan University start-up funds (KYQD(ZR)1854 and KYQD(ZR)1857) are also appreciated.

Experimental section

General Information

The reactions were carried out in schlenk tubes of 25 mL under N_2 atmosphere. Reagents were used as received unless otherwise noted, and solvents were purified according to standard operation procedure. Column chromatography was performed using Silica Gel 60 (300–400 mesh). The reactions were monitored by GC and GC-MS, GC-MS results were recorded on GC-MS QP 2010, and GC analysis was

performed on GC 2014. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Brucker ADVANCE III spectrometer at 400 MHz, 100 MHz and 162 MHz respectively, and chemical shifts were reported in parts per million (ppm). The HR-MS was obtained using a Q-TOF instrument equipped with ESI source, and the mass analyzer type is TOF for EI. All solvents and reagents were purchased from Tansoole, Meryer, Heowns, Energy Chemical, Alfa Aesar, and Aladdin.

Experimental Procedure

In an oven dried 25 mL Schlenk tube was charged with benzyl ammonium triflates **1** (0.2 mmol), P(O)H compounds **2** (0.24 mmol, if it is liquid, add it after charging N_2), $Pd(OAc)_2$ (0.006 mmol, 3 mol %), DPPF (0.008 mmol, 4 mol %) and K_2CO_3 (0.4 mmol, 2.0 equiv), after charging N_2 for three times, dioxane (2.0 mL) was added. The reaction mixture was reacted at 100 °C for 4 h. After completion of the reaction, the reaction mixture was concentrated under vacuum. The desired product was isolated by column chromatography over silica gel (300-400 mesh) using petroleum ether-ethyl acetate as eluent.

Diisopropyl benzylphosphonate (**3a**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 2:1 (v:v) to afford a colorless oil in 91% yield (46.6 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.30–7.28 (m, 4H), 7.25–7.21 (m, 1H), 4.63–4.56 (m, 2H), 3.11 (d,

J = 17.2 Hz, 2H), 1.27 (d, J = 4.8 Hz, 6H), 1.16 (d, J = 5.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.7 (d, J_{C-P} = 8.9 Hz), 129.6 (d, J_{C-P} = 6.6 Hz), 128.1 (d, J_{C-P} = 2.9 Hz), 126.5 (d, J_{C-P} = 3.5 Hz), 70.3 (d, J_{C-P} = 6.9 Hz), 34.5 (d, J_{C-P} = 138.8 Hz), 23.7 (d, J_{C-P} = 27.9 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.6. This compound is known [3e], CAS number: 1083-98-3.

Diethyl benzylphosphonate (**3b**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 2:1 (v:v) to afford a colorless oil in 90% yield (41.1 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.32–7.28 (m, 4H), 7.26–7.22 (m, 1H), 4.06–3.95 (m, 4H), 3.15 (d, J = 17.2 Hz, 2H), 1.23 (t, J = 5.8 Hz, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$): 131.4 (d, J_{C-P} = 7.3 Hz), 129.6 (d, J_{C-P} = 5.3 Hz), 128.4 (d, J_{C-P} = 2.4 Hz), 126.7 (d, J_{C-P} = 2.8 Hz), 62.0 (d, J_{C-P} = 5.4 Hz), 33.6 (d, J_{C-P} = 109.9 Hz), 16.2 (d, J_{C-P} = 4.8 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.5. This compound is known [3e], CAS number: 1080-32-6.

Dibutyl benzylphosphonate (**3c**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 2:1 (v:v) to afford a colorless oil in 94% yield (53.4 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.31–7.28 (m, 4H), 7.25–7.21 (m, 1H), 3.98–3.89 (m, 4H), 3.15 (d,

J = 17.2 Hz, 2H), 1.58–1.53 (m, 4H), 1.36–1.29 (m, 4H), 0.89 (t, J = 5.8 Hz, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$): 131.4 (d, J_{C-P} = 7.3 Hz), 129.6 (d, J_{C-P} = 5.2 Hz), 128.3 (d, J_{C-P} = 2.4 Hz), 126.6 (d, J_{C-P} = 2.9 Hz), 65.6 (d, J_{C-P} = 5.5 Hz), 33.4 (d, J_{C-P} = 110.0 Hz), 32.3 (d, J_{C-P} = 4.8 Hz), 18.5, 13.4.; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.4. This compound is known [9a], CAS number: 3762-27-4.

Ethyl benzyl(phenyl)phosphinate (**3d**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 2:1 (v:v) to afford a colorless oil in 95% yield (49.4 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.55–7.50 (m, 2H), 7.45–7.40 (m, 1H), 7.34–7.29 (m, 2H), 7.14–7.10 (m, 3H), 7.02–6.99 (m, 2H), 4.05–3.95 (m, 1H), 3.86–3.76 (m, 1H), 3.21 (d, J = 18.0 Hz, 2H), 1.20 (t, J = 7.2 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): 132.2 (d, J_{C-P} = 2.8 Hz), 131.9 (d, J_{C-P} = 9.5 Hz), 131.4 (d, J_{C-P} = 7.6 Hz), 130.1 (d, J_{C-P} = 124.9 Hz), 129.9 (d, J_{C-P} = 5.7 Hz), 128.3 (d, J_{C-P} = 9.4 Hz), 128.2 (d, J_{C-P} = 6.0 Hz), 126.6 (d, J_{C-P} = 3.5 Hz), 60.9 (d, J_{C-P} = 6.6 Hz), 38.1 (d, J_{C-P} = 94.8 Hz), 16.4 (d, J_{C-P} = 6.4 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.9. This compound is known [9a], CAS number: 2129-79-5.

Benzyldiphenylphosphine oxide (**3e**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether:

ethyl acetate = 1:1 (v:v) to afford a white solid in 91% yield (53.2 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.71–7.67 (m, 4H), 7.52–7.49 (m, 2H), 7.43–7.42 (m, 4H), 7.18–7.17 (m, 3H), 7.12–7.10 (m, 2H), 3.65 (d, J = 13.2 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 132.3 (d, J_{C-P} = 78.7 Hz), 131.7 (d, J_{C-P} = 2.1 Hz), 131.1 (d, J_{C-P} = 7.3 Hz), 130.1 (d, J_{C-P} = 4.1 Hz), 128.4 (d, J_{C-P} = 9.3 Hz), 128.3 (d, J_{C-P} = 1.9 Hz), 126.7 (d, J_{C-P} = 2.4 Hz), 38.1 (d, J_{C-P} = 53.0 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.4. This compound is known [3e], CAS number: 2959-74-2.

Benzyl di-p-tolylphosphine oxide (**3f**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 94% yield (60.2 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.50–7.45 (m, 4H), 7.14–7.07 (m, 7H), 7.03–7.01 (m, 2H), 3.52 (d, J = 13.6 Hz, 2H), 2.27 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$): 141.9 (d, J_{C-P} = 2.8 Hz), 131.9 (d, J_{C-P} = 10.2 Hz), 131.4 (d, J_{C-P} = 7.8 Hz), 131.0 (d, J_{C-P} = 9.4 Hz), 130.0 (d, J_{C-P} = 5.2 Hz), 129.1 (d, J_{C-P} = 102.8 Hz), 129.0 (d, J_{C-P} = 12.0 Hz), 128.2 (d, J_{C-P} = 2.5 Hz), 126.5 (d, J_{C-P} = 3.0 Hz), 38.1 (d, J_{C-P} = 66.3 Hz), 21.0 (d, J_{C-P} = 0.6 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.7. This compound is known [16], CAS number: 54441-76-8.

Benzyl(butyl)(phenyl)phosphine oxide (**3g)**

The title compound was prepared according to the general experimental procedure

and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 93% yield (50.6 mg), m.p. 102.0-104.0 ^{o}C. ^{1}H NMR (400 M, $CDCl_3$): δ 7.53–7.48 (m, 2H), 7.46–7.42 (m, 1H), 7.38–7.36 (m, 2H), 7.20–7.10 (m, 3H), 7.02–7.00 (m, 2H), 3.30–3.18 (m, 2H), 1.95–1.74 (m, 2H), 1.58–1.48 (m, 1H), 1.38–1.22 (m, 3H), 0.77 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 131.8 (d, J_{C-P} = 7.2 Hz), 131.7 (d, J_{C-P} = 92.5 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 130.7 (d, J_{C-P} = 8.6 Hz), 130.0 (d, J_{C-P} = 5.0 Hz), 128.5 (d, J_{C-P} = 2.6 Hz), 128.4 (d, J_{C-P} = 11.0 Hz), 126.7 (d, J_{C-P} = 2.9 Hz), 38.9(d, J_{C-P} = 61.9 Hz), 27.9 (d, J_{C-P} = 69.1 Hz), 24.0 (d, J_{C-P} = 14.5 Hz), 23.2 (d, J_{C-P} = 4.2 Hz), 13.5.; ^{31}P NMR (162 MHz, $CDCl_3$): δ 38.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{17}H_{21}OP$: 273.1408, found: 273.1405.

(4-Methoxybenzyl)diphenylphosphine oxide (**3i**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 89% yield (57.4 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.64–7.59 (m, 4H), 7.45–7.41 (m, 2H), 7.38–7.33 (m, 4H), 6.96–6.93 (m, 2H), 6.65 (d, J = 8.8 Hz, 2H), 3.66 (s, 3H), 3.52 (d, J = 13.2 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 158.5 (d, J_{C-P} = 2.8 Hz), 132.3 (d, J_{C-P} = 98.0 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 131.1 (d, J_{C-P} = 8.9 Hz), 131.0 (d, J_{C-P} = 5.3 Hz), 128.4 (d, J_{C-P} = 12.5 Hz), 122.8 (d, J_{C-P} = 8.0 Hz), 113.8 (d, J_{C-P} = 2.4 Hz), 55.1, 37.1 (d, J_{C-P} = 67.1 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.6. This compound is known [3e], CAS number:

16114-90-2.

(4-Methylbenzyl)diphenylphosphine oxide (**3j**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 93% yield (57.0 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.64–7.59 (m, 4H), 7.44–7.40 (m, 2H), 7.37–7.32 (m, 4H), 6.91 (br, 4H), 3.54 (d, J = 13.6 Hz, 2H), 2.18 (d, J = 2 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$): 136.3 (d, J_{C-P} = 3.2 Hz), 132.4 (d, J_{C-P} = 98.5 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 131.1 (d, J_{C-P} = 9.0 Hz), 129.9 (d, J_{C-P} = 5.3 Hz), 129.0 (d, J_{C-P} = 2.5 Hz), 128.4 (d, J_{C-P} = 10.6 Hz), 127.8 (d, J_{C-P} = 8.0 Hz), 37.6 (d, J_{C-P} = 66.6 Hz), 21.0.; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.4. This compound is known [6], CAS number: 53144-71-1.

(4-(Tert-butyl)benzyl)diphenylphosphine oxide (**3k**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 81% yield (56.4 mg), m.p. 248.4-248.7 ^{o}C. ^{1}H NMR (400 M, $CDCl_3$): δ 7.64–7.59 (m, 4H), 7.42–7.38 (m, 2H), 7.36–7.31 (m, 4H), 7.12 (d, J = 8.4 Hz, 2H), 6.95 (dd, J = 8.4, 2.0 Hz, 2H), 3.54 (d, J = 13.6 Hz, 2H), 1.16 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$): 149.5 (d, J_{C-P} = 3.1 Hz), 132.4 (d, J_{C-P} = 98.1 Hz), 131.6 (d, J_{C-P} = 2.6 Hz), 131.1 (d, J_{C-P} = 9.1 Hz), 129.7 (d, J_{C-P} = 5.2 Hz), 128.3 (d, J_{C-P} = 11.6 Hz), 127.8 (d, J_{C-P} = 8.0 Hz), 125.3 (d, J_{C-P} = 2.5

Hz), 37.4 (d, J_{C-P} = 66.6 Hz), 34.3, 31.2.; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{25}OP$: 349.1721, found: 349.1716.

(3-Methylbenzyl)diphenylphosphine oxide (**3l**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 94% yield (57.6 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.64–7.59 (m, 4H), 7.44–7.40 (m, 2H), 7.37–7.33 (m, 4H), 6.99–6.96 (m, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.84 (s, 1H), 6.78 (d, *J* = 7.2 Hz, 1H), 3.54 (d, *J* = 13.6 Hz, 2H), 2.14 (s, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$): 137.8 (d, J_{C-P} = 1.4 Hz), 132.4 (d, J_{C-P} = 97.1 Hz), 131.7 (d, J_{C-P} = 1.4 Hz), 131.1 (d, J_{C-P} = 8.7 Hz), 130.9 (d, J_{C-P} = 4.9 Hz), 130.8 (d, J_{C-P} = 7.2 Hz), 128.3 (d, J_{C-P} = 11.4 Hz), 128.1 (d, J_{C-P} = 1.1 Hz), 127.5 (d, J_{C-P} = 1.9 Hz), 127.0 (d, J_{C-P} = 4.9 Hz),38.1 (d, J_{C-P} = 65.8 Hz), 21.2.; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.6. This compound is known [6], CAS number: 23896-92-6.

(2-Methylbenzyl)diphenylphosphine oxide (**3m**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 78% yield (47.8 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.61–7.56 (m, 4H), 7.45–7.41 (m, 2H), 7.37–7.32 (m, 4H), 7.03-6.99 (m, 2H), 6.92–6.85 (m, 2H), 3.58 (d, *J* = 14.0 Hz, 2H), 2.06 (s, 3H).; ^{13}C NMR (100 MHz,

$CDCl_3$): 137.4 (d, J_{C-P} = 5.4 Hz), 132.4 (d, J_{C-P} = 97.8 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 131.1 (d, J_{C-P} = 9.1 Hz), 130.6 (d, J_{C-P} = 4.6 Hz), 130.3 (d, J_{C-P} = 2.1 Hz), 129.6 (d, J_{C-P} = 8.1 Hz), 128.4 (d, J_{C-P} = 11.6 Hz), 126.9 (d, J_{C-P} = 3.2 Hz), 125.6 (d, J_{C-P} = 2.9 Hz), 35.2 (d, J_{C-P} = 66.3 Hz), 20.0 (d, J_{C-P} = 1.1 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.6. This compound is known [3e], CAS number: 158871-10-4.

(Benzo[d][1,3]dioxol-5-ylmethyl)diphenylphosphine oxide (**3n**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 95% yield (63.9 mg), m.p. 227.2-227.4 ^{o}C. ^{1}H NMR (400 M, $CDCl_3$): δ 7.65–7.60 (m, 4H), 7.45–7.35 (m, 6H), 6.58-6.53 (m, 2H), 6.45 (d, J = 8.0 Hz, 1H), 5.80 (s, 2H), 3.50 (d, J = 13.2 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 147.5 (d, J_{C-P} = 1.8 Hz), 146.5 (d, J_{C-P} = 2.7 Hz), 132.8, 131.8 (d, J_{C-P} = 3.1 Hz), 131.1 (d, J_{C-P} = 8.9 Hz), 128.5 (d, J_{C-P} = 11.5 Hz), 124.4 (d, J_{C-P} = 8.2 Hz), 123.3 (d, J_{C-P} = 5.8 Hz), 110.5 (d, J_{C-P} = 4.6 Hz), 108.1 (d, J_{C-P} = 2.2 Hz), 100.9, 37.6 (d, J_{C-P} = 66.9 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.4. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{20}H_{17}O_3P$: 337.0994, found: 337.0990.

(Naphthalen-2-ylmethyl)diphenylphosphine oxide (**3o**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 74% yield (50.7 mg). ^{1}H NMR (400

M, $CDCl_3$): δ 7.76–7.69 (m, 5H), 7.67–7.65 (m, 2H), 7.57 (s, 1H), 7.52–7.48 (m, 2H), 7.44–7.40 (m, 6H), 7.25–7.22 (m, 1H), 3.81 (d, J = 10.8 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 133.3 (d, J_{C-P} = 2.1 Hz), 132.3 (d, J_{C-P} = 78.7 Hz), 132.2 (d, J_{C-P} = 1.5 Hz), 131.8 (d, J_{C-P} = 2.1 Hz), 131.2 (d, J_{C-P} = 7.2 Hz), 128.9 (d, J_{C-P} = 5.3 Hz), 128.7 (d, J_{C-P} = 6.5 Hz), 128.5 (d, J_{C-P} = 9.7 Hz), 128.1 (d, J_{C-P} = 3.4 Hz), 127.9 (d, J_{C-P} = 1.5 Hz), 127.6 (d, J_{C-P} = 0.6 Hz), 127.5 (d, J_{C-P} = 1.0 Hz), 125.9, 125.6 (d, J_{C-P} = 0.8 Hz), 38.4 (d, J_{C-P} = 52.7 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.3. This compound is known [3e], CAS number: 935659-31-7.

Diphenyl(4-vinylbenzyl)phosphine oxide (**3p**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 69% yield (43.9 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.65–7.59 (m, 4H), 7.45–7.41 (m, 2H), 7.38–7.34 (m, 4H), 7.15 (d, J = 8.0 Hz, 2H), 6.99 (dd, J = 8.2, 1.8 Hz, 2H), 6.56 (dd, J = 19.4, 12.8 Hz, 1H), 5.59 (d, J = 17.6 Hz, 1H), 5.11 (d, J = 10.8 Hz, 1H), 3.57 (d, J = 13.6 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 136.4 (d, J_{C-P} = 1.4 Hz), 136.1 (d, J_{C-P} = 4.2 Hz), 132.7, 131.8 (d, J_{C-P} = 2.7 Hz), 131.1 (d, J_{C-P} = 9.1 Hz), 130.7 (d, J_{C-P} = 8.2 Hz), 130.2 (d, J_{C-P} = 5.3 Hz), 128.5 (d, J_{C-P} = 11.6 Hz), 126.2 (d, J_{C-P} = 2.7 Hz), 113.6, 37.9 (d, J_{C-P} = 66.0 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.3. This compound is known [17], CAS number: 741-41-3.

(4-Fluorobenzyl)diphenylphosphine oxide. (**3q**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 91% yield (56.5 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.70–7.66 (m, 4H), 7.53–7.50 (m, 2H), 7.46–7.43 (m, 4H), 7.08–7.05 (m, 2H), 6.88 (t, J = 6.8 Hz, 2H), 3.61 (d, J = 10.8 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 161.9 (d, J_{C-P} = 197.8 Hz), 132.1 (d, J_{C-P} = 78.9 Hz), 131.9 (d, J_{C-P} = 2.2 Hz), 131.5 (dd, J = 6.4, 4.1 Hz), 131.1 (d, J_{C-P} = 7.2 Hz), 128.5 (d, J_{C-P} = 9.3 Hz), 126.8 (dd, J = 6.3, 2.6 Hz), 115.3 (dd, J = 20.6, 3.5 Hz), 37.2 (d, J_{C-P} = 53.0 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.2 (d, J_{P-F} = 4.05 Hz). This compound is known [12], CAS number: 1393677-42-3.

4-((Diphenylphosphoryl)methyl)benzonitrile (**3r**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 80% yield (50.8 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.64–7.58 (m, 4H), 7.49–7.44 (m, 2H), 7.41–7.36 (m, 6H), 7.15 (dd, J = 8.4, 2.0 Hz, 2H), 3.62 (d, J = 13.6 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 137.1 (d, J_{C-P} = 8.0 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 132.0 (d, J_{C-P} = 2.6 Hz), 131.5 (d, J_{C-P} = 99.7 Hz), 131.0 (d, J_{C-P} = 9.4 Hz), 130.8 (d, J_{C-P} = 5.1 Hz), 128.7 (d, J_{C-P} = 11.7 Hz), 118.7 (d, J_{C-P} = 1.8 Hz), 110.7 (d, J_{C-P} = 3.0 Hz), 38.4 (d, J_{C-P} = 64.0 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.9. This compound is known [12], CAS number: 18629-19-1.

Diphenyl(4-(trifluoromethyl)benzyl)phosphine oxide (**3s**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 87% yield (62.7 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.64–7.59 (m, 4H), 7.47–7.43 (m, 2H), 7.39–7.35 (m, 6H), 7.15 (d, J = 7.6 Hz, 2H), 3.62 (d, J = 13.6 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 135.5 (dd, J_{C-P} = 9.0, 1.0 Hz), 132.0 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 99.4 Hz), 131.0 (d, J_{C-P} = 9.1 Hz), 130.3 (d, J_{C-P} = 5.0 Hz), 129.0 (dd, J_{C-P} = 32.2, 1.0 Hz), 128.6 (d, J_{C-P} = 11.8 Hz), 125.2-125.1 (m), 124.1 (q, J_{C-P} = 269.4 Hz), 38.0 (d, J_{C-P} = 64.8 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.0. This compound is known [12], CAS number: 220396-39-4.

(4-Chlorobenzyl)diphenylphosphine oxide (**3t**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 88% yield (57.5 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.71–7.67 (m, 4H), 7.54–7.50 (m, 2H), 7.47–7.43 (m, 4H), 7.16 (d, J = 6.4 Hz, 2H), 7.05-7.03 (m, 2H), 3.61 (d, J = 10.8 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 132.8 (d, J_{C-P} = 2.9 Hz), 132.0 (d, J_{C-P} = 79.1 Hz), 131.9 (d, J_{C-P} = 2.2 Hz), 131.3 (d, J = 4.2 Hz), 131.1 (d, J_{C-P} = 7.3 Hz), 129.7 (d, J_{C-P} = 6.5 Hz), 128.6 (d, J_{C-P} = 9.3 Hz), 128.5 (d, J_{C-P} = 2.1 Hz), 37.5 (d, J_{C-P} = 52.6 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.0. This compound is known [3e], CAS number: 53144-72-2.

(2-Chlorobenzyl)diphenylphosphine oxide (**3u**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 85% yield (55.5 mg), m.p. 110.3-111.5 ^{o}C. ^{1}H NMR (400 M, $CDCl_3$): δ 7.65–7.61 (m, 4H), 7.47–7.35 (m, 7H), 7.15–7.04 (m, 3H), 3.79 (d, J = 14.0 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 134.2 (d, J_{C-P} = 6.8 Hz), 132.1 (d, J_{C-P} = 99.1 Hz), 131.9 (d, J_{C-P} = 4.3 Hz), 131.8 (d, J = 2.4 Hz), 131.1 (d, J_{C-P} = 9.3 Hz), 129.7 (d, J_{C-P} = 7.3 Hz), 129.3 (d, J_{C-P} = 1.9 Hz), 128.4 (d, J_{C-P} = 11.7 Hz), 128.2 (d, J_{C-P} = 2.5 Hz), 126.8 (d, J_{C-P} = 2.0 Hz), 34.6 (d, J_{C-P} = 66.4 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{16}ClOP$: 327.0706, Found: 327.0701.

(3,4-Dichlorobenzyl)diphenylphosphine oxide (**3v**)

The title compound was prepared according to the general experimental procedure and purified by column chromatography on silica gel and eluted with petroleum ether: ethyl acetate = 1:1 (v:v) to afford a white solid in 83% yield (59.9 mg). ^{1}H NMR (400 M, $CDCl_3$): δ 7.64–7.59 (m, 4H), 7.47–7.43 (m, 2H), 7.40–7.35 (m, 4H), 7.16 (d, J = 8.0 Hz, 1H), 7.08–7.07 (m, 1H), 6.89 (dt, J = 8.4, 2.0 Hz, 1H), 3.50 (d, J = 13.2 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): 132.2 (d, J_{C-P} = 3.1 Hz), 132.0 (d, J_{C-P} = 3.7 Hz), 131.8 (d, J_{C-P} = 5.3 Hz), 131.6 (d, J_{C-P} = 99.4 Hz), 131.5 (d, J = 7.9 Hz), 131.0 (d, J_{C-P} = 3.2 Hz), 130.9 (d, J_{C-P} = 9.1 Hz), 130.1 (d, J_{C-P} = 2.5 Hz), 129.3 (d, J_{C-P} = 5.0 Hz),

128.6 (d, $J_{C\text{-}P}$ = 11.7 Hz), 37.2 (d, $J_{C\text{-}P}$ = 65.1 Hz).; ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.8. This compound is known [18], CAS number: 101894-92-2.

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In this study, we present the first palladium-catalyzed phosphorylation of benzyl ammonium triflates with P(O)H compounds. Various benzylphosphorus compounds were produced in good to excellent yields with high functional group tolerance. All the three kinds of hydrogen phosphoryl compounds, i.e. H-phosphonates, H-phosphinates and secondary phosphine oxides, were applicable to this reaction. The succesful scale-up experiment and one-pot synthetic operation also well demonstrated its practicality.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: