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Efficient potassium hydroxide promoted P-arylation of aryl halides with diphenylphosphine

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ABSTRACT

A simple synthetic method of triarylphosphine compounds by KOH-promoted P-Arylation reaction of aryl halides with diphenylphosphine is presented. Notably, this transformation could smoothly proceed with high yields under transition-metal-free and mild reaction conditions. In addition, this protocol is valuable for industrial application due to the convenient operation and readily accessible aromatic halides. A possible explanation of the reaction mechanism was proposed based on the experimental data.

Triarylphosphines are a type of chemical materials and fine chemicals with high added value. Because of their unique structure, properties and extensive application, they are widely used in catalysis, flame retardant materials, optical materials and other fields. [1] At present, many methods can be used to synthesize triarylphosphines. The most frequently employed method for their preparations is treatment of electrophilic phosphorus reagents with organometallic reagents, [2] which lacks tolerance for functional groups. In the 1980s, Hirao and co-workers described the first example of aryl and vinyl halide couplings with dialkyl phosphites under catalyst Pd(0). [3] Following this, remarkable progress in the development of Csp^2–P bond formation by cross-coupling has been reported in the past decades, containing various methods via transition metal-catalyzed direct activation of the P-X (X = halogen [4], CN^5, B^6, Bi^7, N^8, O^9, S^{10}, Si^{11} etc.) and P–$H^{4a,}$[5-11] (Si^{4b}; Sn^{4c}) bond. These studies provide efficient synthetic routes for triarylphosphines, but toxic and expensive metal catalysts, such as palladium, nickel and gold, must be used. Therefore, developing novel and convenient synthetic methods for triarylphosphine compounds is still of great significance. To the best of our knowledge, constructions of C-P bond by transition-metal-free coupling reaction are scarce, and highly-active intermediates Ar_2P-M (M = Li, Na, K) needs to be prepared in advance, however, this method lacks convenience [12].

In this paper, we report a novel approach of triarylphosphine by P-arylation reactions of aryl halides and diphenylphosphine with the participation of potassium hydroxide. The transition-metal-free condition, simple technology, easy to get raw materials, and high yields are the advantages of this present method.

C-P bond coupling reaction using transition-metal catalysts is an important method for the synthesis of arylphosphine compounds, and the catalysts play decisive role in such reactions. However, it was unexpectedly found that (4-methoxyphenyl) diphenylphosphine **2e** was successfully obtained from 4-methoxy iodobenzene and diphenylphosphine (Ph_2PH) using DMF as solvent without any other chemical reagents, and the product was characterized by NMR and HRMS. Although the yield of this reaction was very low (13 %), it was a very interesting phenomenon because of the transition metal-free condition and worthy of further research.

For this purpose, we optimized the conditions of the reaction, and the reaction of 4-methoxybenzyl bromide and Ph_2PH was used as a model reaction. The results were shown in Table 1. Considering that the removed small molecule hydrogen bromide may affect the reaction process, various bases were investigated. It was clear that when KOH was used, the reaction yield was the highest and could be reached 80 %. (entry 4) The reaction could also take place in the presence of other bases, and the yields of the target product were 20 % ~ 35 %. (entries 1-3)

Subsequently, different solvents were investigated. It was found that the solvent had great influence on the reaction. DMSO and DMF had no difference in yields, however, DMF was the better choice because of the foul smell of heated DMSO. (entries 4-5) Other solvents, such as 1,4-dioxane and THF, could hardly promote the reaction. (entries 6-7) Other affecting factors including reactant mole ratio, reaction time and reaction temperature were investi-

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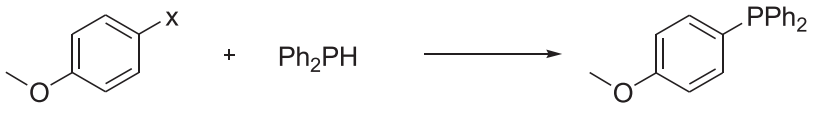
0022-328X/

Table 1
Optimization of the Reaction Conditions[a]



2e

Entry	X	Base/eq.	Ph_2PH/eq.	Solvent	Yield/% [b]
1	Br	K_2CO_3/0.6	1.05	DMF	35
2	Br	Pyridine/1.2	1.05	DMF	27
3	Br	Et_3N/1.2	1.05	DMF	20
4	Br	KOH/1.2	1.05	DMF	80
5	Br	KOH/1.2	1.05	DMSO	78
6	Br	KOH/1.2	1.05	THF	NR
7	Br	KOH/1.2	1.05	1,4-Dioxane	NR
8	Br	KOH/1.2	1.5	DMF	79
9	Br	KOH/1.5	1.05	DMF	80
10	Br	KOH/1.5	1.5	DMF	77
11	I	KOH/1.2	1.05	DMF	87
12	Cl	KOH/1.2	1.05	DMF	12
13	F	KOH/1.2	1.05	DMF	trace

gated respectively. The results showed that the yields could not be improved by increasing the mole ratio of base, prolonging the reaction time and increasing the reaction temperature. (entries 8-10) Eventually, we determined that the optimized condition was aryl halide (1 eq.), Ph_2PH (1.05 eq.) and KOH (1.2 eq.) in solvent DMF at 110 °C. Finally, under optimized conditions, we studied the reactivity of different halogenated aromatic compounds and the results showed that the reactivity of aryl halides followed the order I > Br > F > Cl. (entry 4 and entries 11-13)

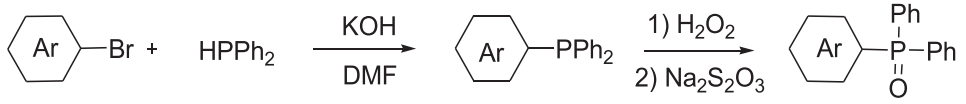
In order to study the scope of the reaction, a series of aryl halides with different substituent groups were investigated. Because trivalent phosphorus was sensitive to air, the products were treated with oxidant, in order to reduce the influence of post-treatment on the reaction yields. In addition, the more available bromoaromatics were used as the reaction substrate. The results are presented in Table 2. In all cases, aryl bromide substituted with electron-donating or electron-withdrawing groups underwent the reaction smoothly and gave products in high yields. It is clear that the efficiency of the reaction was rarely dependent on the electronic nature of the substrates. (**3a**-**3h**) As for substrates **3i-3k**, it turned out that steric hindrance slightly affected the reaction efficiency.

The reaction of heteroaromatic bromides and Ph_2PH under the optimized conditions was also explored. The results (Table 3) showed that the corresponding products were generated in excellent yield using 2-bromopyridine and 2-bromobenzopyridine as starting materials, but no target products were obtained when 2-bromothiophene and 2-bromobenzothiophene were used.

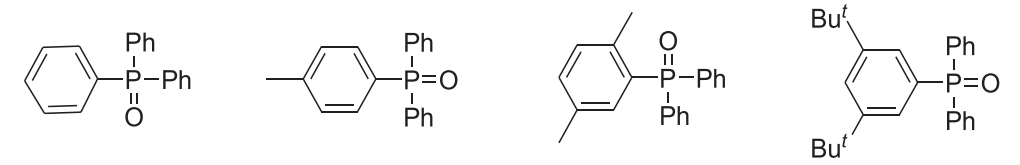
Product **8** can also be easily synthesized in this way. In order to demonstrate the practical application of this method, a gram-scale reaction was designed with 4-bromobenzoic acid under the standard conditions. The corresponding compound 4-(diphenylphosphanyl) benzoic acid was obtained in an isolated yield of 82 % (Scheme 1).

According to the reported literature and all our knowledge in organophosphorus chemistry, the reaction was most likely via a substituation process of nucleophile Ph_2PK, [12] which was from the deprotonation of Ph_2PH. In order to confirm this, Ph_2PH reacting with KOH was carried out, obviously, the reaction solution gradually changed from colorless to red, which was the color of the dilute solution of Ph_2PK. In spite of no Ph_2PK being detected by ^{31}P NMR spectroscopy, it was probable that due to the concentration was below the lowest limit of NMR detection. (Scheme 2.1, see SI) Moreover, another interesting result was discovered, the target product **2a** could be obtained by the reaction of **1a** and Ph_2PH in DMF without adding KOH. (Scheme 2.2) This showed that there was another reaction process in the reaction, it was quite possible that this path occured through the intermediate triarylphos-

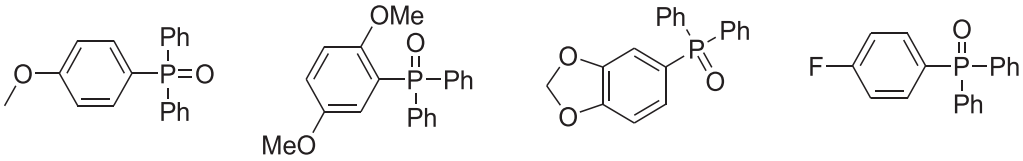
Table 2
Scope of reaction for bromoaromatics and diphenylphosphine [a]



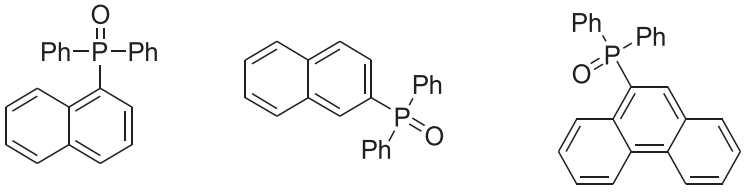
1 2 3



3a, 80 % **3b**, 81 % **3c**, 76 % **3d**, 65 %

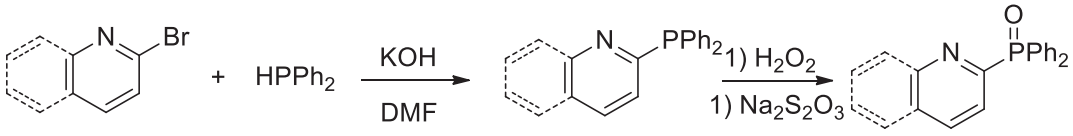


3e, 78 % **3f**, 79 % **3g**, 85 % **3h**, 86 %



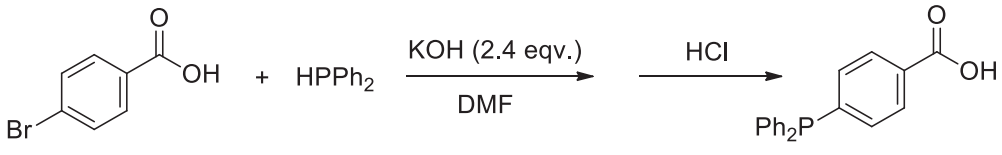
3i, 75 % **3j**, 69 % **3k**, 77 %

Table 3
Scope of reaction for heteroaromatic bromides and diphenylphosphine [a]



4 5 6

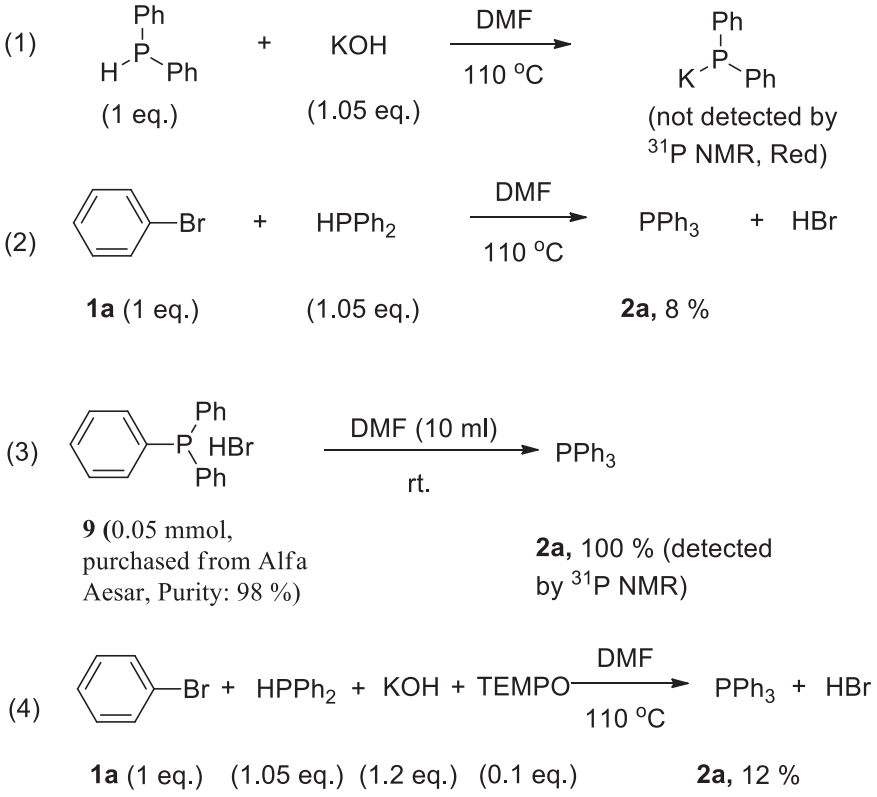
6a, 90 % **6b**, 87 %



7

8, 80 **%** (milligram-scale)
82 **%** (gram-scale)

Scheme 1. Large-scale synthesis



Scheme 2. Control experiments

phonium bromide **9**. [13] Unfortunately, **9** was not be detected by ^{31}P NMR spectroscopy because it readily decomposed in DMF solution. (Scheme 2.3) It is possible that the generated HBr inhibited the further conversion of reactant. Another phenomenon was that when 0.1 equivalent of TEMPO was added to the reaction system, the yield was only 12% after 12 hours. This showed that the product was mainly generated by free radical process, and other pathways also contribute to the replacement reaction.

Based on the above experimental results and relevant literature, a possible mechanism was proposed, as shown in Scheme 3. There were probably two main reaction processes in this reaction. *Route a.* Ph_2PK was generated by the reaction of Ph_2PH and KOH. The $[ArBr]^{-\bullet}$ radical anion was first generated by a single electron transfer (SET) reaction with Ph_2PK, and then it breaks down into the radical $Ar^{\bullet}$ and the anion Br^{-}. Radical $Ar^{\bullet}$ combines covalently with nucleophile Ph_2P^{-} to form the radical anion $[ArPPh_2]^{-\bullet}$. It transfers an electron to ArBr to afford the coupling product $ArPPh_2$ and regenerates the radical anion $[ArBr]^{-\bullet}$. *Route b.* First, nucleophile Ph_2PH added to aryl bromide to form zwitterionic intermediate **10**. Then, bromine was eliminated to restore the aromaticity of the ring and furnished phosphonium salt. In both steps, DMF may form hydrogen bond with bromide to facilitate the addition of Ph_2PH and the elimination of bromide. Subsequently, the target product was generated via removing one molecule of HBr.

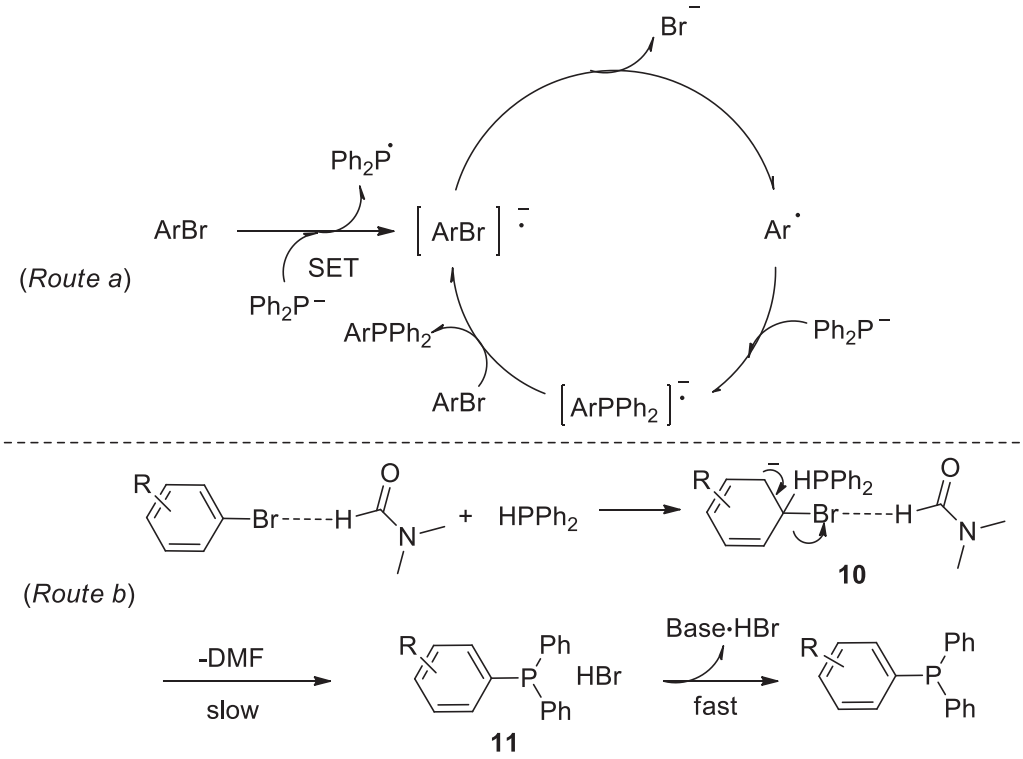
In Han's work, the yields of the coupling products using Ph_2PNa and aryl halides follow the increasing order of ArI < ArBr < ArCl = ArF,[12a] the result is very different from this method. This phenomena is due to the presence of side product **12** $(Ph_2P)_2$ through the halogen–metal exchange reaction. It is possible that low concentrations of Ph_2PK is more favorable to the replacement reaction than this competing pathway. Scheme 4.

In conclusion, we have developed an economic and efficient synthetic protocol of triarylphosphine compounds using halogenated aromatic and diphenylphosphine with the assistance of potassium hydroxide. The reaction proceeded smoothly to synthesis of arylphosphine with easy operation and high efficiency. Moreover, possible mechanistic pathways were given for this new reaction.

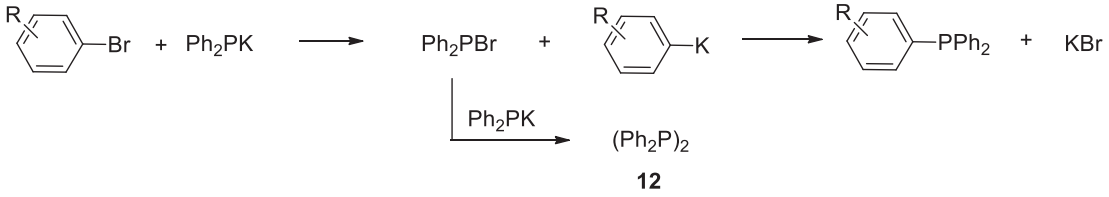
^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker 300M and 400M spectrometer. Chemical shifts are expressed in ppm from internal TMS (^{1}H and ^{13}C). All coupling constants (*J* values) are reported in Hertz (Hz). HRMS were obtained on an Agilent 1290-6540 Q-Tof spectrometer by electrospray ionization (ESI). All air- and moisture-sensitive manipulations were carried out under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. Dry N,N-Dimethylformamide (Purity: 99.9%) was purchased from Alfa Aesar; Diphenylphosphine was purchased from Aladdin; Silica gel (200-300 mesh) purchased from Qingdao Hai Yang Chemical Industry Co. Ltd. was used for chromatographic separations. Other chemicals and solvents were purchased from commercial companies and used as received.

2. (4-methoxyphenyl)diphenylphosphine (2e); procedure

In a 25 mL schlenk bottle was stirred a mixture of **1e** (374 mg, 2 mmol), Ph_2PH (391 mg, 2.1 mmol) in DMF (10 mL) under a nitrogen atmosphere at room temperature, then, KOH (135 mg, 2.4 mmol) was added and the mixture was warmed to 110°C and kept stirring for 10 h. After cooling to room temperature, the mixture was diluted with water and extracted with CH_2Cl_2. The organic phase was washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated. After removing the solvents under the reduced pressure, the resulting solid was subjected to silica gel column chromatography (10:1 petroleum ether/CH_2Cl_2 as an eluent). white solid (467 mg, 2.15 mmol, 80 % yield), ^{31}P{1H} NMR (121 MHz, CDCl3) δ = -7.1; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.83 (s, 3H), 6.90-6.94 (m, 2H), 7.27-7.37 (m, 12H); ^{13}C NMR (75 MHz,



Scheme 3. Proposed reaction mechanism



Scheme 4. competing reaction

$CDCl_3$) δ = 55.21 (s, CH_3), 114.26 (d, J_{CP} = 8.3 Hz, 2CH), 127.62 (d, J_{CP} = 8.3 Hz, C), 128.44 (d, J_{CP} = 6 Hz, 4CH), 133.44 (d, J_{CP} = 18.7 Hz, 4CH), 135.64 (d, J_{CP} = 21 Hz, 2CH), 137.90 (d, J_{CP} = 9.7 Hz, C), 160.39 (s, C); HRMS: Calcd. for $C_{19}H_{17}OP[M + H^+]$ 293.1095, Found: 293.1096.

3. Aryldiphenylphosphine oxide (3); general procedure

In a 25 mL schlenk bottle was stirred a mixture of **1** (2 mmol), Ph_2PH (391 mg, 2.1 mmol) in DMF (10 mL) under a nitrogen atmosphere at room temperature, then, KOH (135 mg, 2.4 mmol) was added and the mixture was warmed to 110°C and kept stirring for about 12 h until total consumption of the starting material 1 as monitored by gas chromatography. After cooling to room temperature, then a 30 % H_2O_2 aqueous solution (2 mL) was slowly added. After stirring for 10 min, the mixture was quenched with $Na_2S_2O_3$ aqueous solution (20 ml). The mixture was diluted with water and extracted with CH_2Cl_2. The organic phase was washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated. After removing the solvents under the reduced pressure, the target product was subjected to silica gel column chromatography (5:1 CH_2Cl_2/AcOEt as an eluent).

4. Triphenylphosphine oxide (3a)

white solid (445 mg, 1.60 mmol, 80 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.48 (m, 6H), 7.52-7.54 (m, 3H), 7.65-7.70 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 128.49 (d, J_{CP} = 12 Hz, 6CH), 131.92 (d, J_{CP} = 3 Hz, 3CH), 132.10 (d, J_{CP} = 9 Hz, 6CH), 132.62 (d, J_{CP} = 103 Hz, 3C); HRMS: Calcd. for $C_{18}H_{15}OP[M + H^+]$ 279.0939, Found: 279.0941.

5. Diphenyl(p-tolyl)phosphine oxide (3b)

white solid (473 mg, 1.62 mmol, 81 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.39 (s, 3H), 7.25-7.29 (m, 2H), 7.41-7.46 (m, 5H), 7.49-7.58 (m, 5H), 7.64-7.69 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.58 (s, CH_3), 128.43 (d, J_{CP} = 12 Hz, 4CH), 129.25 (d, J_{CP} = 13 Hz, 2CH), 129.25 (d, J_{CP} = 106 Hz, C), 131.78 (s, CH), 131.81 (s, CH), 132.06 (d, J_{CP} = 9 Hz, 4CH), 132.07 (s, CH), 132.17 (s, CH), 132.91 (d, J_{CP} = 104 Hz, C), 142.42 (d, J_{CP} = 2 Hz, C); HRMS: Calcd. for $C_{19}H_{17}OP[M + H^+]$ 293.1095, Found: 293.1093.

6. (2, 5-Dimethylphenyl)diphenylphosphine oxide (3c)

white solid (465 mg, 1.52 mmol, 76 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.20 (s, 3H), 2.37 (s, 3H), 6.87-6.91 (m, 1H), 7.14-7.17 (m, 1H), 7.21-7.24 (m, 1H), 7.44-7.48 (m, 4H), 7.51-7.56 (m, 2H), 7.63-7.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.97 (s, CH_3), 21.21 (d, J_{CP} = 5 Hz, CH_3), 128.50 (d, J_{CP} = 12 Hz, 4CH), 130.44 (d, J_{CP} = 102 Hz, C), 131.40(d, J_{CP} =3 Hz, 2CH), 131.86 (d, J_{CP} = 9 Hz, CH), 131.96 (d, J_{CP} = 10 Hz, 4CH), 132.81 (d, J_{CP} = 3 Hz, CH), 132.96 (d, J_{CP} = 103 Hz, 2C), 133.95 (d, J_{CP} = 12 Hz, CH),

134.68 (d, J_{CP} = 13 Hz, C), 140.02 (J_{CP} = 8 Hz, C); HRMS: Calcd. for $C_{20}H_{19}OP[M + H^+]$ 307.1252, Found: 307.1255.

7. (3, 5-Di-tert-butylphenyl)diphenylphosphine oxide (3d)

white solid (507 mg, 1.30 mmol, 65 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.27 (s, 18H), 7.43-7.45 (m, 5H), 7.52-7.55 (m, 3H), 7.59-7.60 (m, 1H), 7.66-7.71 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.29 (s, CH_3), 35.02 (s, C), 126.06 (d, J_{CP} = 3 Hz, CH), 126.38 (d, J_{CP} = 10 Hz, 2CH), 128.35 (d, J_{CP} = 12 Hz, 4CH), 131.21 (d, J_{CP} = 100 Hz, C), 131.74 (s, 2CH), 132.09 (d, J_{CP} = 10 Hz, 4CH), 133.12 (d, J_{CP} = 102 Hz, 2C), 150.99 (d, J_{CP} = 12 Hz, 2C); HRMS: Calcd. for $C_{26}H_{31}OP[M + H^+]$ 391.2191, Found: 391.2187.

8. (4-Methoxyphenyl)diphenylphosphine oxide (3e)

white solid (480 mg, 1.56 mmol, 78 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.83 (s, 3H), 6.95-6.98 (m, 2H), 7.42-7.47 (m, 4H), 7.50-7.61 (m, 4H), 7.64-7.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.34 (s, CH_3), 114.12 (d, J_{CP} = 13 Hz, 2CH), 123.58 (d, J_{CP} = 110 Hz, C), 128.44 (d, J_{CP} = 12 Hz, 4CH), 131.80 (d, J_{CP} = 3 Hz, 2CH), 132.05 (d, J_{CP} = 10 Hz, 4CH), 133.49 (d, J_{CP} = 104 Hz, 2C), 133.97 (d, J_{CP} = 12 Hz, 2CH), 162.55 (d, J_{CP} = 3 Hz, C); HRMS: Calcd. for $C_{19}H_{17}O_2P[M + H^+]$ 309.1044, Found: 309.1046.

9. (2, 5-Dimethoxyphenyl)diphenylphosphine oxide (3f)

white solid (534 mg, 1.58 mmol, 79 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.45 (s, 3H), 3.79 (s, 3H), 6.84-6.87 (m, 1H), 7.05-7.08 (m, 1H), 7.40-7.44 (m, 7H), 7.69-7.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 55.79 (s, CH_3), 55.94 (s, CH_3), 113.18 (d, J_{CP} = 8 Hz, CH), 118.87 (d, J_{CP} = 4 Hz, CH), 120.35 (d, J_{CP} = 2 Hz, CH), 121.20 (d, J_{CP} = 102 Hz, C), 128.09 (d, J_{CP} = 12 Hz, 4CH), 131.50 (d, J_{CP} = 3 Hz, 2CH), 131.85 (d, J_{CP} = 10 Hz, 4CH), 133.66 (d, J_{CP} = 107 Hz, 2C), 153.90 (d, J_{CP} = 14 Hz, C), 154.75 (d, J_{CP} = 3 Hz, C); HRMS: Calcd. for $C_{20}H_{19}O_3P[M + H^+]$ 339.1150, Found: 339.1150.

10. Benzo[d][1,3]dioxol-5-yldiphenylphosphine oxide (3g)

white solid (548 mg, 1.70 mmol, 85 % yield), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.00 (s, 2H), 6.85-6.89 (m, 1H), 7.06-7.09 (m, 1H), 7.15-7.21 (m, 1H), 7.43-7.47 (m, 4H), 7.51-7.55 (m, 2H), 7.64-7.69 (m, 4H); ^{13}C NMR (100 MHz, CDCl3): δ = 101.62 (s, CH_2), 108.64 (d, J_{CP} = 16 Hz, CH), 111.56 (d, J_{CP} = 12 Hz, CH), 125.73 (d, J_{CP} = 107 Hz, C), 127.59 (d, J_{CP} = 10 Hz, CH), 128.48 (d, J_{CP} = 11 Hz, 4CH), 131.89 (d, J_{CP} = 3 Hz, 2CH), 132.05 (d, J_{CP} = 10 Hz, 4CH), 132.76 (d, J_{CP} = 104 Hz, 2C), 148.00 (d, J_{CP} = 18 Hz, C), 150.87 (d, J_{CP} = 3 Hz, C); HRMS Calcd. for $C_{19}H_{15}O_3P$ $[M + H^+]$ 323.0837, Found: 323.0839.

11. (4-Fluorophenyl)diphenylphosphine oxide (3h)

white solid (509 mg, 1.72 mmol, 86 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12-7.17 (m, 2H), 7.44-7.49 (m, 4H), 7.52-7.57 (m, 2H), 7.63-7.71 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 115.88 (dd, J_1 = 21 Hz, J_1 = 3 Hz, 2CH), 128.58 (d, J_{CP} = 12 Hz, 4CH), 128.65 (dd, J_{CP} = 106 Hz, J_{CF} = 3 Hz, C) 132.0 (d, J_{CP} = 10 Hz, 4CH), 132.07 (d, J_{CP} = 4 Hz, 2CH), 132.37 (d, J_{CP} = 104 Hz, 2C), 134.57 (dd, J_1 = 11 Hz, J_1 = 9 Hz, 2CH), 165.06 (dd, J_{CF} = 252 Hz, J_{CP} = 3 Hz, C); HRMS: Calcd. for $C_{18}H_{14}FOP[M + H^+]$ 297.0845, Found: 297.0848.

12. Naphthalen-1-yldiphenylphosphine oxide (3i)

white solid (492 mg, 1.50 mmol, 75 % yield), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27-7.56 (m, 10H), 7.66-7.71 (m, 4H), 7.87-7.90 (m, 1H), 8.00-8.02 (m, 1H), 8.58-8.60 (m, 1H); ^{13}C NMR (100 MHz, CDCl3): δ = 124.14 (d, J_{CP} = 14 Hz, CH), 126.51 (s, CH), 127.35 (s, CH), 127.66 (d, J_{CP} = 6 Hz, CH), 128.59 (d, J_{CP} = 12 Hz, 4CH), 128.77 (s, CH), 128.99 (d, J_{CP} = 102 Hz, C), 131.89 (d, J_{CP} = 3 Hz, 2CH), 132.11 (d, J_{CP} = 10 Hz, 4CH), 132.92 (d, J_{CP} = 103 Hz, 2C), 133.28 (d, J_{CP} = 3 Hz, CH), 133.76 (d, J_{CP} = 11 Hz, CH), 133.78 (d, J_{CP} = 6 Hz, C), 133.94 (d, J_{CP} = 9 Hz, C); HRMS Calcd. for $C_{22}H_{17}OP$ $[M + H^+]$ 329.1095, Found: 329.1092.

13. Naphthalen-2-yldiphenylphosphine oxide (3j)

white solid (453 mg, 1.38 mmol, 69 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.74 (m, 13H), 7.85-7.91 (m, 3H), 8.27 (d, J_{HH} = 16 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 126.84 (d, J_{CP} = 10 Hz, CH), 126.99 (s, CH), 127.85 (s, CH), 128.30 (s, CH), 126.36 (d, J_{CP} = 11 Hz, CH), 128.58 (d, J_{CP} = 12 Hz, 4CH), 128.99 (s, CH), 129.52 (d, J_{CP} = 105 Hz, C), 132.01 (d, J_{CP} = 4 Hz, 2CH), 132.16 (d, J_{CP} = 10 Hz, 4CH), 132.45 (d, J_{CP} = 13 Hz, C), 132.51 (d, J_{CP} = 103 Hz, 2C), 134.04 (d, J_{CP} = 9 Hz, CH), 134.75 (d, J_{CP} = 2 Hz, C); HRMS: Calcd. for $C_{22}H_{17}OP[M + H^+]$ 329.1095, Found: 329.1092.

14. Phenanthren-9-yldiphenylphosphine oxide (3k)

white solid (582 mg, 1.54 mmol, 77 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42-7.49 (m, 5H), 7.51-7.56 (m, 3H), 7.58-7.77 (m, 8H), 8.64-8.69 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 122.66 (s, CH), 123.06 (s, CH), 127.04 (s, CH), 127.21 (d, J_{CP} = 5 Hz, 2CH), 127.92 (d, J_{CP} = 101 Hz, C), 128.67 (d, J_{CP} = 12 Hz, 4CH), 128.76 (d, J_{CP} = 6 Hz, CH), 129.15 (s, CH), 130.06 (s, CH), 130.19 (d, J_{CP} = 110 Hz, C), 130.19 (d, J_{CP} = 103 Hz, C), 130.51 (d, J_{CP} = 8 Hz, C), 131.99 (s, CH), 132.02 (s, CH), 132.18 (d, J_{CP} = 9 Hz, CH), 132.17 (d, J_{CP} = 9 Hz, 4CH), 133.25 (s, C), 136.80 (s, C), 136.92 (s, C); HRMS: Calcd. for $C_{26}H_{19}OP[M + H^+]$ 379.1252, Found: 379.1253.

15. Diphenyl(pyridin-2-yl)phosphine oxide (6a)

white solid (502 g, 1.80 mmol, 90 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.53 (m, 7H), 7.81-7.91 (m, 5H), 8.29-8.32 (m, 1H), 8.77 (d, J_{HH} = 4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 125.28 (d, J_{CP} = 3 Hz, CH), 128.35 (d, J_{CP} = 12 Hz, 4CH), 128.37 (d, J_{CP} = 19 Hz, CH), 131.90 (d, J_{CP} = 2 Hz, 2CH), 132.16 (d, J_{CP} = 9 Hz, 4CH), 132.18 (d, J_{CP} = 104 Hz, 2C), 136.21 (d, J_{CP} = 9 Hz, CH), 150.13 (d, J_{CP} = 19 Hz, CH), 156.39 (d, J_{CP} = 131 Hz, C); HRMS: Calcd. for $C_{17}H_{14}NOP[M + H^+]$ 280.0891, Found: 280.0895.

16. Diphenyl(quinolin-2-yl)phosphine oxide (6b)

white solid (573 g, 1.74 mmol, 87 % yield), ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41-7.51 (m, 6H), 7.56-7.60 (m, 1H), 7.70-7.74 (m, 1H), 7.82-7.84 (m, 1H), 7.97-8.03 (m, 4H), 8.14-8.16 (m, 1H), 8.27-8.31 (m, 1H), 8.35-8.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 123.37 (d, J_{CP} = 22 Hz, CH), 127.89 (s, CH), 128.17 (s, CH), 128.32 (d, J_{CP} = 12 Hz, 4CH), 130.05 (s, CH), 130.32 (s, CH), 131.81 (d, J_{CP} = 3 Hz, 2CH), 132.23 (d, J_{CP} = 9 Hz, 4CH), 132.56 (d, J_{CP} = 103 Hz, 2C), 136.17 (d, J_{CP} = 9 Hz, CH), 148.04 (s, C), 148.25 (s, C), 157.20 (d, J_{CP} = 129 Hz, C); HRMS: Calcd. for $C_{21}H_{16}NOP[M + H^+]$ 330.1048, Found: 330.1043.

17. 4-(Diphenylphosphino)benzoic acid (8); Procedure

In a 250 mL schlenk bottle was stirred a mixture of 7 (4.02 g, 20 mmol), 2 (3.91 g, 21 mmol) in DMF (150 mL) under a nitrogen atmosphere at room temperature, then, KOH (1.35 g, 24 mmol) was added and the mixture was warmed to 110 °C and keep stirring

for 24 h. After cooling to room temperature, the mixture was acidified with a 2 M HCl aqueous solution (until pH = 2-3). Then, the mixture was diluted with water and extracted with CH_2Cl_2. The organic phase was washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated. After removing the solvents under the reduced pressure, the resulting solid was subjected to silica gel column chromatography (AcOEt as an eluent). white solid (499 g, 1.64 mmol, 82 % yield), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.38 (m, 1H), 8.02-8.04 (m, 2H); ^{13}C NMR (100 MHz, CDCl3): δ = 128.74 (d, J_{CP} = 8 Hz, 4CH), 129.09 (s, C), 129.24 (s, 2CH), 129.87 (d, J_{CP} = 6 Hz, 2CH), 133.19 (d, J_{CP} = 18 Hz, 2CH), 134.04 (d, J_{CP} = 20 Hz, 4CH), 136.04 (d, J_{CP} = 10 Hz, 2C), 150.53 (d, J_{CP} = 15 Hz, C), 171.95 (s, COOH); HRMS Calcd. for $C_{19}H_{15}O_2P$ [M + H^+] 305.0888, Found: 305.0891.

Declaration of Competing Interest

None

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2021.121932.

References

[1] (a) P.J. Murphy, organophosphorus reagents oxford university press, Oxford, U.K, 2004; (b) T. Baumgartner, R. Réau, 2006 Chem. Rev., 106 4681–4727; (c) V. Iaroshenko, organophosphorus chemistry: from molecules to applications Wiley-VCH Verlag GmbH, 2019.
[2] For selected examples: (a) M. Elarda, J. Denis, M. Ferreira, H. Bricout, D. Landy, S. Tilloya, E. Monflier, Catal. Today 247 (2015) 47–54; (b) D.E. Bergbreiter, Y.-C. Yang, J. Org. Chem. 75 (2010) 873–878.
[3] T. Hirao, T. Masunaga, Y. Ohshiro, T. Agawa, Tetrahedron Lett 21 (1980) 3595–3598.
[4] For selected examples: (a) A.J. Bloomfield, S.B. Herzon, Org. Lett. 14 (2012) 4370–4373; (b) M. Sun, Y.-S. Zang, L.-K. Hou, X.-X. Chen, W. Sun, S.-D. Yang, Eur. J. Org. Chem. (2014) 6796–6801; (c) S.E. Martıń, M. Bonaterra, R.A. Rossi, J. Organomet. Chem. 664 (2002) 223–227; (d) T. Ghosh, P. Maity, D. Kundu, B.C. Ranu, New J. Chem. 40 (2016) 9556–9564.
[5] (a) J.-S. Zhang, T.-Q. Chen, J. Yang, L.-B. Han, Chem. Commun. 51 (2015) 7540; (b) M. Sun, H.-Y. Zhang, Q. Han, K. Yang, S.-D. Yang, Chem. Eur. J. 17 (2011) 9566–9570.
[6] (a) G.-B. Hu, W.-Z. Chen, T.-T. Fu, Z.-M. Peng, H.-W. Qiao, Y.-X. Gao, Y.-F. Zhao, Org. Lett. 15 (2013) 5362–5365; (b) T.-T. Fu, H.W. Qiao, Z.M. Peng, G.B. Hu, X.J. Wu, Y.X. Gao, Y.X. Zhao, Org. Biomol. Chem. 12 (2014) 2895–2902.
[7] T. Wang, S. Sang, L. Liu, H.-W. Qiao, Y-X. Gao, Y.-F. Zhao, J. Org. Chem. 79 (2014) 608–617.
[8] (a) B. Yang, Z.X. Wang, J. Org. Chem. 84 (2019) 1500–1509; (b) Y. He, H.M. Wu, F.D. Toste, Chem. Sci. 6 (2015) 1194–1198; (c) R. Berrino, S. Cacchi, G. Fabrizi, A. Goggiamani, P. Stabile, Org. Biomol. Chem. 8 (2010) 4518–4520.
[9] For selected examples: (a) C.-R. Shen, G.-Q. Yang, W.-B. Zhang, Org. Biomol. Chem. 10 (2012) 3500–3505; (b) J. Yang, Q. Chen, L.-B. Han, J. Am. Chem. Soc. 137 (2015) 1782–1785; (c) Y.-L. Zhao, G.-J. Wu, F.-S. Han, Chem. Commun. 48 (2012) 5868–5870.
[10] J. Yang, J. Xiao, T.-Q. Chen, S.-F. Yin, L.-B. Han, Chem. Commun. 52 (2016) 12233–12236.
[11] H.-Q. Luo, H.-D. Liu, X.-W. Chen, K.-K. Wang, X.-Z. Luo, K.-J. Wang, Chem. Commun. 53 (2017) 956–958.
[12] (a) J.-J. Ye, J.-Q. Zhang, Y. Saga, S.-Y. Onozawa, S. Kobayashi, K. Sato, N. Fukaya, L.-B. Han, Organometallics 39 (2020) 2682–2694; (b) L. Hintermann, T.T. Dang, A. Labonne, T. Kribber, L. Xiao, P. Naumov, Chem. Eur. J. 15 (2009) 7167–7179; (c) A.M. Aguiar, H.J. Greenberg, K.E. Rubenstein, J. Org. Chem. 28 (1963) 2091–2093.
[13] W.-H. Huang, C.-H. Zhong, ACS Omega 4 (2019) 6690–6696.