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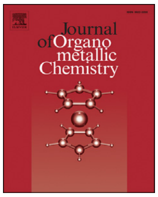

Note

Nickel-catalyzed phosphorylation of aryl triflates with P(O)–H compounds

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ABSTRACT

A nickel-catalyzed phosphorylation of aryl triflates with P(O)–H compounds is disclosed. This reaction can proceed smoothly under a mild reaction condition, producing the corresponding aryl phosphorus compounds in good to high yields.

1. Introduction

The development of efficient methods for preparing aryl phosphorus compounds is of great importance because of their wide application in medicinal chemistry, materials chemistry and organic synthesis [1]. Though transition metal-catalyzed phosphorylation of aryl halides and counterparts with P(O)–H compounds pioneered by Hirao's group has been well established [2], great efforts are devoted to making the cross coupling greener by replacing the aryl halides and noble metal catalysts with cheaper, more readily available and less toxic participants [3,4]. Recently, the scope of Hirao reaction has been extended to use phenol derivatives as the substrate [5,6]. Aryl triflates, mesylates and tosylates readily coupled with P(O)–H compounds in the presence of a noble palladium catalyst, serving as an efficient procedure for P–C bonds formation [5]. Herein, we report an efficient nickel-catalyzed phosphorylation of aryl triflates to produce the corresponding aryl phosphorous compounds in good to high yields under a mild reaction condition (Scheme 1) [6].

2. Result and discussion

We initiated our work with examining the reactivity of phenyl triflate **1a** and diphenylphosphine oxide **2a** mediated by a nickel/phosphine catalyst, and the obtained results were compiled in Table 1. In the presence of 10 mol% $Ni(COD)_2$ (bis(1,5-cyclooctadiene)nickel(0))/dcype ($Cy_2PCH_2CH_2PCy_2$), the reaction took place to give the coupling product **3a** and its reduced form **3a'** in 81% combined yield (entry 1). Other selected phosphines also mediated the reaction with 1,1′-bis(diphenylphosphino)-ferrocene (dppf) being the best choice (entries 2–6). The phosphine ligand was essential to this transformation. In the absence of phosphine ligand, the yield dramatically decreased to 19% (entry 7). Na_2CO_3 was found as active as K_2CO_3. However, a stronger base led to decrease of yield (entries 9 and 10), which would be ascribed to the strong hydrolysis of triflate under the reaction conditions. This reaction also took place smoothly in toluene and DMF (entries 11 and 13), whereas hexane was used as the solvent, poor yield was afforded (entry 12). The Nickel catalyst is crucial to this reaction. No reaction was observed in the absence of the catalyst (entry 14). When the reaction was performed at 60 °C, 80% yield of **3a** was given under similar reaction conditions (entry 15).

Under the optimized reaction conditions, the substrate scope was investigated. As shown in Table 2, a variety of aryl triflates **1**

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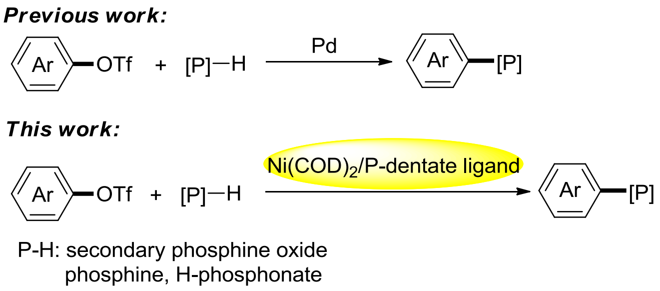
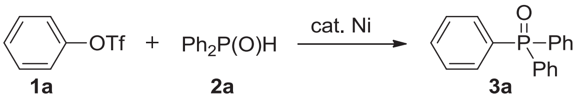


Scheme 1. Nickel-catalyzed phosphorylation of aryl triflates.

Table 1
Nickel-catalyzed phosphorylation of phenyl triflate.[a]



Entry	Cat. Ni	Ligand	Base	Solvent	Yield (**3a**/**3a'**)[b]
1	Ni(COD)$_2$	dcype	K_2CO_3	Dioxane	81%(97/3)
2	Ni(COD)$_2$	PCy$_3$	K_2CO_3	Dioxane	66%(67/33)
3	Ni(COD)$_2$	dppp	K_2CO_3	Dioxane	75%(97/3)
4	Ni(COD)$_2$	dppb	K_2CO_3	Dioxane	88%(98/2)
5	Ni(COD)$_2$	dppf	K_2CO_3	Dioxane	99%(99/1)
6	Ni(COD)$_2$	BINAP	K_2CO_3	Dioxane	35%(73/27)
7	Ni(COD)$_2$	none	K_2CO_3	Dioxane	19%(49/51)
8	Ni(COD)$_2$	dppf	Na_2CO_3	Dioxane	99%(99/1)
9	Ni(COD)$_2$	dppf	Cs_2CO_3	Dioxane	35%(77/23)
10	Ni(COD)$_2$	dppf	*t*-BuONa	Dioxane	n.d.
11	Ni(COD)$_2$	dppf	Na_2CO_3	Toluene	88%(98/2)
12	Ni(COD)$_2$	dppf	Na_2CO_3	Hexane	39%(95/5)
13	Ni(COD)$_2$	dppf	Na_2CO_3	DMF	89%(98/2)
14	none	none	Na_2CO_3	Dioxane	n.d.
15[c]	Ni(COD)$_2$	dppf	Na_2CO_3	Dioxane	80%(98/2)

[a] Reaction conditions: **1a** (0.2 mmol), $Ph_2P(O)H$ (0.2 mmol), 10 mol% Ni(COD)$_2$, base (0.2 mmol), solvent (2 mL), 80 °C, 20 h.

[b] GC yield using tridecane as an internal standard.

[c] 60 °C.

coupled with hydrogen phosphoryl compounds **2** to produce the corresponding products in good to high yields. High yields were obtained with both electron-rich and electron-deficient aryl triflates (entries 2–8). Thus, derivatives of aryl triflates bearing an electron-donating group like methyl (2-, 3- and 4-position), methoxy and phenyl group on the benzene ring all gave the coupling products in good yields (entries 2–6). Aryl-F and Aryl-CN bonds which could be cleaved by nickel catalyst survived well under the present reaction conditions (entries 7 and 8). Substrate with an electron-withdrawing CF_3 group also coupled with **2a**, furnishing the product **3i** in 79% yields (entry 9). High yield of **3j** was obtained from the reaction of naphthyl triflate **1j** with **2a** (entry 10). *N*-heterocyclic triflates **1k** also showed high reactivity in the catalytic system, generating the coupling product **3k** in 85% yield.

Other hydrogen phosphoryl compounds are also applicable to this transformation. In addition to diphenylphosphine oxide **2a**, aliphatic *n*-$Bu_2P(O)H$ (Table 2, entry 12), the bulky *t*-BuPhP(O)H (entry 13) and $Cy_2P(O)H$ (entry 14) coupled with phenyl triflate **1a** readily by elevating the reaction temperature, producing the corresponding products in moderate to high yields. Similarly, diisopropyl phosphite **2e** also served as a good substrate, affording the product **3o** in 70% yield (1.5 equiv **2e** was added due to partly hydrolytic decomposition of phosphoryl group, entry 15). Worth noting is that the highly coordinative diphenylphosphine could also be used as the substrate to produce the expected triphenylphosphine **3a'** in 84% yield under similar reaction conditions (entry 16) [7].

On the basis of the previous literatures [6,8], a plausible mechanism was proposed as shown in Scheme 2. Ni(0) complex **A** firstly oxidatively adds to aryl triflates to produce species **B**, which undergoes ligand exchange with hydrogen phosphoryl compounds by the aid of a base, giving the intermediate **C**. Reductive elimination of **C** produces the corresponding coupling product **3** and regenerates complex **A**.

3. Conclusion

In summary, we have developed an efficient nickel-catalyzed phosphorylation of aryl triflates with hydrogen phosphoryl compounds. A variety of aryl phosphorus compounds are produced under a mild reaction condition from the readily available starting materials. This reaction is well complementary to the previous nickel-catalyzed P—C bonds formation from phenol derivatives [6].

4. Experimental section

4.1. General information

All reactions were carried out in the oven-dried Schlenck tubes under a N_2 atmosphere. Dry solvents were obtained by purification according to standard methods. Reagents were used as received unless otherwise noted. Column chromatography was performed using Silica Gel 60 (particle size 37–54 μm). The pure products were obtained by means of column chromatography. ^1H NMR, ^{13}C NMR and ^{31}P NMR data were acquired on a Bruker-400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C, and 162 MHz for ^{31}P NMR spectroscopy). Chemical shifts for ^1H NMR are referred to internal Me_4Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for ^{31}P NMR were relative to H_3PO_4 (85% solution in D_2O, 0 ppm). Compounds **3a** to **3o** and **3a'** have been reported privously [4g–i,9].

4.2. Synthesis of starting materials

After phenols and pyridine were dissolved in dry DCM, triflic anhydride was added slowly by syringe over 5 min at 0 °C. Then the reaction mixture was allowed to be warmed up to 25 °C and further stirred at 25 °C for 12 h. After the reaction mixture was quenched with water, the aqueous layer was extracted with CH_2Cl_2 and the combined organic layer was dried over Na_2SO_4 and then filtrated. The products were purified by regular flash chromatography (petroleum ether/EtOAc mixtures) [10].

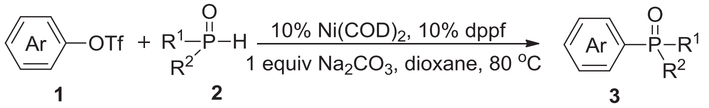
4.3. Typical procedure for the nickel-catalyzed phosphorylation of aryl triflates with P(O)—H compounds

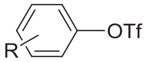
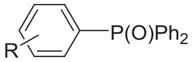
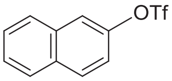
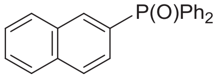
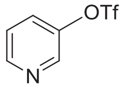
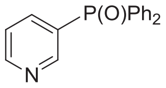
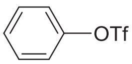
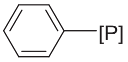
Under a N_2 atmosphere, 0.2 mmol aryl triflate**1a**, 0.2 mmol $Ph_2P(O)H$ **2a**, 10 mol% Ni(COD)$_2$, 10 mol% dppf, 1.0 equiv Na_2CO_3 and 2 mL dioxane were charged into a 10 mL schlenck tube. The mixture was stirred at 80 °C for 20 h. After removal of the volatile, the residues were passed through a short silica chromatography (particle size 37–54 μm, petroleum ether/ethyl acetate as eluent) to afford analytically pure organophosphorus compounds **3**.

4.3.1. Triphenylphosphine oxide (**3a**)

[4h] Purification by chromatography (petroleum ether/EtOAc = 1:1) afforded **3a** (53.4 mg, 96%) as a white solid. $R_f = 0.25$ (petroleum ether/EtOAc = 1:1); ^1H NMR (400 MHz $CDCl_3$): δ 7.69–7.65 (m, 6H), 7.53–7.45 (m, 9H). ^{13}C NMR (100 MHz $CDCl_3$):

Table 2
Ni-catalyzed C–O/P–H cross coupling of aryl triflates **1** with P–H compounds **2**.[a]



entry	substrate **1**	substrate **2**		product **3** (isolated yield)
		$Ph_2P(O)H$	**2a**	
1	**1a**, R = 4-H		**2a**	**3a**, R = 4-H, 96%
2	**1b**, R = 2-Me		**2a**	**3b**, R = 2-Me, 76%
3	**1c**, R = 3-Me		**2a**	**3c**, R = 3-Me, 92%
4	**1d**, R = 4-Me		**2a**	**3d**, R = 4-Me, 87%
5	**1e**, R = 4-MeO		**2a**	**3e**, R = 4-MeO, 85%
6	**1f**, R = 4-Ph		**2a**	**3f**, R = 4-Ph, 90%
7	**1g**, R = 4-F		**2a**	**3g**, R = 4-F, 91%
8	**1h**, R = 4-CN		**2a**	**3h**, R = 4-CN, 86%
9[b]	**1i**, R = 4-CF_3		**2a**	**3i**, R = 4-CF_3, 79%
10	 **1j**		**2a**	 **3j,** 88%
11	 **1k**		**2a**	 **3k,** 85%
				
12[b]	**1a**	*n*-$Bu_2P(O)H$	**2b**	**3l**, [P] = *n*-$Bu_2P(O)$, 90%
13[b]	**1a**	*t*-BuPhP(O)H	**2c**	**3m**, [P] = *t*-BuPhP(O), 78%
14[b]	**1a**	$Cy_2P(O)H$	**2d**	**3n**, [P] = $Cy_2P(O)$, 56%
15[b,c]	**1a**	(*i*-PrO)$_2$P(O)H	**2e**	**3o**, [P] = (*i*-PrO)$_2$P(O), 70%
16[d]	**1a**	Ph_2PH	**2f**	**3a`**, [P] = Ph_2P, 84%

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), 10 mol% Ni(COD)$_2$, base (0.2 mmol), 2 mL dioxane, 80 °C, 20 h.
[b] 100 °C. [c] 1.5 equiv **2**. [d] 120 °C.

δ 132.50(d, $J_{C\text{-}P}$ = 104.8 Hz), 132.09 (d, $J_{C\text{-}P}$ = 9.8 Hz), 131.96 (d, $J_{C\text{-}P}$ = 2.8 Hz), 128.52 (d, $J_{C\text{-}P}$ = 12.0 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 29.18 ppm.

4.3.2. *Triphenylphosphine (**3a'**)*

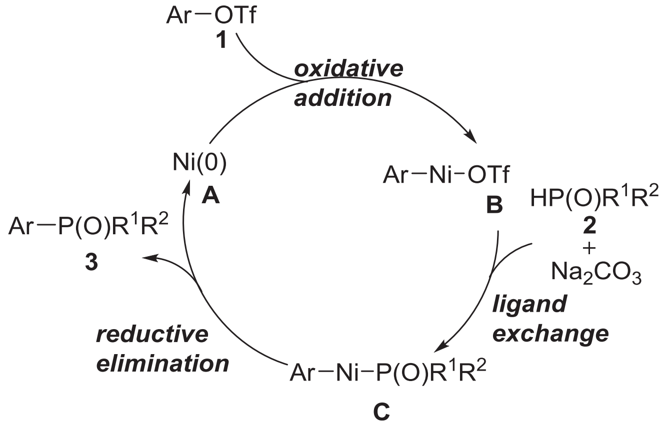
[4h] Purification by chromatography (petroleum ether) afforded **3a'** (44.0 mg, 84%) as a white solid. R_f = 0.43 (petroleum ether); ^{1}H NMR (400 MHz $CDCl_3$): δ 7.317 (br, 15H). ^{13}C NMR (100 MHz $CDCl_3$): δ 137.23 (d, $J_{C\text{-}P}$ = 10.7 Hz), 133.80 (d, $J_{C\text{-}P}$ = 19.4 Hz), 128.77, 128.56 (d, $J_{C\text{-}P}$ = 6.9 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ −5.42 ppm.

4.3.3. *Diphenyl(o-tolyl)phosphine oxide (**3b**)*

[4h] Purification by chromatography (petroleum ether/EtOAc = 1:1) afforded **3b** (44.4 mg, 76%) as a white solid. R_f = 0.34 (petroleum ether/EtOAc = 1:1);^{1}H NMR (400 MHz $CDCl_3$): δ 7.65 (dd, J = 7.6 Hz, J = 12.0 Hz,4H), 7.54 (t, J = 7.6 Hz, 2H), 7.48–7.40 (m,5H), 7.28 (d, J = 6.8 Hz, 1H), 7.12 (dd, J = 6.4 Hz, J = 6.4 Hz, 1H),7.03 (dd, J = 7.8 Hz, J = 14.0 Hz, 1H),2.45 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 143.30 (d, $J_{C\text{-}P}$ = 8.0 Hz), 133.49 (d, $J_{C\text{-}P}$ = 12.9 Hz), 132.68 (d, $J_{C\text{-}P}$ = 103.9 Hz), 132.14 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.06 (d, $J_{C\text{-}P}$ = 19.8 Hz), 131.91 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.82 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.73 (d, $J_{C\text{-}P}$ = 102.5 Hz), 128.59 (d, $J_{C\text{-}P}$ = 12.0 Hz), 125.21 (d, $J_{C\text{-}P}$ = 12.8 Hz), 21.70 (d, $J_{C\text{-}P}$ = 4.7 Hz). ^{31}P NMR (162 MHz $CDCl_3$): δ 31.86 ppm.

4.3.4. *Diphenyl(m-tolyl)phosphine oxide (**3c**)*

[4h] Purification by chromatography (petroleum ether/EtOAc = 1:1) afforded **3c** (53.7 mg, 92%) as a white solid. R_f = 0.41 (petroleum ether/EtOAc = 1:1); ^{1}H NMR (400 MHz $CDCl_3$): δ 7.67 (dd, J = 7.6 Hz, J = 12.0 Hz, 4H), 7.58–7.53 (m, 3H), 7.48–7.44 (m, 4H), 7.40–7.35 (m, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz $CDCl_3$): δ 138.50 (d, $J_{C\text{-}P}$ = 11.9 Hz), 132.61 (d, $J_{C\text{-}P}$ = 103.4 Hz), 132.81 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.51 (d, $J_{C\text{-}P}$ = 9.4 Hz), 132.21 (d, $J_{C\text{-}P}$ = 103.2 Hz), 132.10 (d, $J_{C\text{-}P}$ = 9.9 Hz), 131.92 (d, $J_{C\text{-}P}$ = 2.7 Hz), 129.19 (d, $J_{C\text{-}}$



Scheme 2. A proposed mechanism for the nickel-catalyzed phosphorylation of aryl triflates.

$_{\text{P}}$ = 10.3 Hz), 128.50 (d, $J_{\text{C-P}} = 12.0$ Hz), 128.33 (d, $J_{\text{C-P}} = 12.8$ Hz), 21.45. ^{31}P NMR (162 MHz CDCl$_3$): δ 29.47 ppm.

4.3.5. *Diphenyl(p-tolyl)phosphine oxide (**3d**)*

[4h] Purification by chromatography (petroleum ether/EtOAc = 1:1) afforded **3d** (50.8 mg, 87%) as a white solid. R$_f$ = 0.28 (petroleum ether/EtOAc = 1:1); ^{1}H NMR (400 MHz CDCl$_3$): δ 7.66 (dd, $J = 7.6$ Hz, $J = 11.6$ Hz, 4H), 7.58–7.52 (m, 4H), 7.47–7.43 (m, 4H), 7.28–7.27 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz CDCl$_3$): δ 142.47 (d, $J_{\text{C-P}} = 2.8$ Hz), 132.83 (d, $J_{\text{C-P}} = 103.5$ Hz), 132.14 (d, $J_{\text{C-P}} = 10.1$ Hz), 132.08 (d, $J_{\text{C-P}} = 9.9$ Hz), 131.84 (d, $J_{\text{C-P}} = 2.7$ Hz), 129.27 (d, $J_{\text{C-P}} = 12.5$ Hz), 129.16 (d, $J_{\text{C-P}} = 106.0$ Hz), 128.46 (d, $J_{\text{C-P}} = 12.1$ Hz), 21.63 (d, $J_{\text{C-P}} = 1.0$ Hz). ^{31}P NMR (162 MHz CDCl$_3$): δ 29.23 ppm.

4.3.6. *(4-Methoxyphenyl)diphenylphosphine oxide (**3e**)*

[4h] Purification by chromatography (petroleum ether/EtOAc = 1:2) afforded **3e** (52.4 mg, 85%) as a white solid. R$_f$ = 0.50 (EtOAc); ^{1}H NMR (400 MHz CDCl$_3$): δ 7.66 (dd, $J = 8.0$ Hz, $J = 12.0$ Hz, 4H), 7.61–7.52 (m, 4H), 7.47–7.44 (m, 4H), 6.97 (d, $J = 7.6$ Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz CDCl$_3$): δ 162.53 (d, $J_{\text{C-P}} = 2.7$ Hz), 133.98 (d, $J_{\text{C-P}} = 11.2$ Hz), 132.89 (d, $J_{\text{C-P}} = 104.0$ Hz), 132.06 (d, $J_{\text{C-P}} = 9.8$ Hz), 131.85 (d, $J_{\text{C-P}} = 2.7$ Hz), 128.48 (d, $J_{\text{C-P}} = 12.0$ Hz), 123.48 (d, $J_{\text{C-P}} = 109.9$ Hz), 114.12 (d, $J_{\text{C-P}} = 13.1$ Hz), 55.37. ^{31}P NMR (162 MHz CDCl$_3$): δ 29.28 ppm.

4.3.7. *[1,1′-Biphenyl]-4-yldiphenylphosphine oxide (**3f**)*

[4h] Purification by chromatography (petroleum ether/EtOAc = 1:1) afforded **3f** (63.7 mg, 90%) as a white solid. R$_f$ = 0.30 (petroleum ether/EtOAc = 1:1); ^{1}H NMR (400 MHz CDCl$_3$): δ 7.77–7.68 (m, 8H), 7.61–7.55 (m, 4H), 7.50–7.44 (m, 6H), 7.41–7.37 (m, 1H). ^{13}C NMR (100 MHz CDCl$_3$): δ 144.79 (d, $J_{\text{C-P}} = 2.8$ Hz), 139.88, 132.65 (d, $J_{\text{C-P}} = 10.2$ Hz), 132.36 (d, $J_{\text{C-P}} = 104.0$ Hz), 132.14 (d, $J_{\text{C-P}} = 9.9$ Hz), 132.08 (d, $J_{\text{C-P}} = 2.7$ Hz), 130.87 (d, $J_{\text{C-P}} = 104.8$ Hz), 129.00, 128.40 (d, $J_{\text{C-P}} = 12.1$ Hz), 128.22, 127.30, 127.24 (d, $J_{\text{C-P}} = 12.4$ Hz). ^{31}P NMR (162 MHz CDCl$_3$): δ 29.59 ppm.

4.3.8. *(4-Fluorophenyl)diphenylphosphine oxide (**3g**)*

[4i] Purification by chromatography (petroleum ether/EtOAc = 1:1) afforded **3g** (53.9 mg, 91%) as a white solid. R$_f$ = 0.36 (petroleum ether/EtOAc = 1:1); ^{1}H NMR (400 MHz CDCl$_3$): δ 7.70–7.63 (m, 6H), 7.58–7.54 (m, 2H), 7.49–7.46 (m, 4H), 7.16 (t, $J = 8.4$ Hz, 2H). ^{13}C NMR (100 MHz CDCl$_3$): δ 165.11 (dd, $J_{\text{C-P}} = 3.2$ Hz, $J_{\text{C-F}} = 252.1$ Hz), 134.61 (dd, $J_{\text{C-P}} = 8.8$ Hz, $J_{\text{C-F}} = 11.3$ Hz), 132.17 (d, $J_{\text{C-P}} = 2.7$ Hz), 132.12 (d, $J_{\text{C-P}} = 104.7$ Hz), 132.03 (d, $J_{\text{C-P}} = 9.9$ Hz), 128.63 (d, $J_{\text{C-P}} = 12.2$ Hz), 128.41 (dd, $J_{\text{C-P}} = 105.5$ Hz, $J_{\text{C-F}} = 3.0$ Hz), 128.40 (dd, $J_{\text{C-P}} = 13.2$ Hz, $J_{\text{C-F}} = 21.3$ Hz). ^{31}P NMR (162 MHz CDCl$_3$): δ 28.82 ppm.

4.3.9. *4-(Diphenylphosphoryl)benzonitrile (**3h**)*

[4g] Purification by chromatography (petroleum ether/EtOAc = 1:1) afforded **3h** (52.1 mg, 86%) as a white solid. R$_f$ = 0.31 (petroleum ether/EtOAc = 1:1); ^{1}H NMR (400 MHz CDCl$_3$): δ 7.83–7.75 (m, 4H), 7.68–7.58 (m, 6H), 7.52–7.48 (m, 4H). ^{13}C NMR (100 MHz CDCl$_3$): δ 138.30 (d, $J_{\text{C-P}} = 98.6$ Hz), 132.65 (d, $J_{\text{C-P}} = 9.4$ Hz), 132.62 (d, $J_{\text{C-P}} = 3.4$ Hz), 132.04 (d, $J_{\text{C-P}} = 12.7$ Hz), 132.02 (d, $J_{\text{C-P}} = 9.9$ Hz), 131.00 (d, $J_{\text{C-P}} = 105.1$ Hz), 128.87 (d, $J_{\text{C-P}} = 12.2$ Hz), 117.90 (d, $J_{\text{C-P}} = 1.3$ Hz), 115.67 (d, $J_{\text{C-P}} = 3.1$ Hz). ^{31}P NMR (162 MHz CDCl$_3$): δ 28.19 ppm.

4.3.10. *Diphenyl(4-(trifluoromethyl)phenyl)phosphine oxide (**3i**)*

[4h] Purification by chromatography (petroleum ether/EtOAc = 1:1) afforded **3i** (54.7 mg, 79%) as a white solid. R$_f$ = 0.31 (petroleum ether/EtOAc = 1:1); ^{1}H NMR (400 MHz CDCl$_3$): δ 7.82 (t, $J = 7.2$ Hz, 2H), 7.74–7.62 (m, 6H), 7.59 (t, $J = 7.2$ Hz, 2H), 7.51–7.49 (m, 4H). ^{13}C NMR (100 MHz CDCl$_3$): δ 137.10 (d, $J_{\text{C-P}} = 100.0$ Hz), 133.56 (dt, $J_{\text{C-P}} = 2.7$ Hz, $J_{\text{C-F}} = 30.2$ Hz), 132.57 (d, $J_{\text{C-P}} = 10.1$ Hz), 132.41 (d, $J_{\text{C-P}} = 2.7$ Hz), 132.04 (d, $J_{\text{C-P}} = 10.0$ Hz), 131.56 (d, $J_{\text{C-P}} = 105.5$ Hz), 128.76 (d, $J_{\text{C-P}} = 12.2$ Hz), 125.31 (dt, $J_{\text{C-P}} = 11.8$ Hz, $J_{\text{C-F}} = 3.1$ Hz), 123.56 (d, $J_{\text{C-F}} = 271.3$ Hz). ^{31}P NMR (162 MHz CDCl$_3$): δ 28.22 ppm.

4.3.11. *Naphthalen-2-yldiphenylphosphine oxide (**3j**)*

[4h] Purification by chromatography (petroleum ether/EtOAc = 1:1) afforded **3j** (57.7 mg, 88%) as a white solid. R$_f$ = 0.29 (petroleum ether/EtOAc = 1:1); ^{1}H NMR (400 MHz CDCl$_3$): δ 8.29 (d, $J = 14.0$ Hz, 1H), 7.91–7.85 (m, 3H), 7.74–7.44 (m, 13H). ^{13}C NMR (100 MHz CDCl$_3$): δ 134.74 (d, $J_{\text{C-P}} = 2.2$ Hz), 134.05 (d, $J_{\text{C-P}} = 9.3$ Hz), 132.45 (d, $J_{\text{C-P}} = 103.7$ Hz), 132.43 (d, $J_{\text{C-P}} = 13.2$ Hz), 132.17 (d, $J_{\text{C-P}} = 9.9$ Hz), 132.07 (d, $J_{\text{C-P}} = 2.8$ Hz), 129.47 (d, $J_{\text{C-P}} = 103.8$ Hz), 128.99, 128.60 (d, $J_{\text{C-P}} = 12.1$ Hz), 128.37 (d, $J_{\text{C-P}} = 10.6$ Hz), 128.32, 127.86 (d, $J_{\text{C-P}} = 0.6$ Hz), 127.01, 126.84 (d, $J_{\text{C-P}} = 10.7$ Hz). ^{31}P NMR (162 MHz CDCl$_3$): δ 29.51 ppm.

4.3.12. *Diphenyl(pyridin-3-yl)phosphine oxide (**3k**)*

[4g] Purification by chromatography (petroleum ether/EtOAc = 1:2) afforded **3k** (47.4 mg, 85%) as a white solid. R$_f$ = 0.33 (EtOAc); ^{1}H NMR (400 MHz CDCl$_3$): δ 8.79–8.78 (m, 2H), 8.05 (t, $J = 9.6$ Hz, 1H), 7.71–7.66 (m, 4H), 7.60–7.43 (m, 7H). ^{13}C NMR (100 MHz CDCl$_3$): δ 152.60 (d, $J_{\text{C-P}} = 1.7$ Hz), 152.49 (d, $J_{\text{C-P}} = 11.8$ Hz), 139.77 (d, $J_{\text{C-P}} = 7.8$ Hz), 132.45 (d, $J_{\text{C-P}} = 2.8$ Hz), 131.97 (d, $J_{\text{C-P}} = 10.1$ Hz), 131.45 (d, $J_{\text{C-P}} = 105.2$ Hz), 129.09 (d, $J_{\text{C-P}} = 100.1$ Hz), 128.79 (d, $J_{\text{C-P}} = 12.3$ Hz), 123.52 (d, $J_{\text{C-P}} = 8.8$ Hz). ^{31}P NMR (162 MHz CDCl$_3$): δ 26.54 ppm.

4.3.13. *Dibutyl(phenyl)phosphine oxide (**3l**)*

[4h] Purification by chromatography (petroleum ether/EtOAc = 1:2) afforded **3l** (42.8 mg, 90%) as a white solid. R$_f$ = 0.53 (EtOAc); ^{1}H NMR (400 MHz CDCl$_3$): δ 7.70 (dd, $J = 8.0$ Hz, $J = 8.0$ Hz, 2H), 7.55–7.49 (m, 3H), 2.02–1.80 (m, 4H), 1.67–1.56 (m, 2H), 1.46–1.33 (m, 6H), 0.89–0.86 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz CDCl$_3$): δ 132.61 (d, $J_{\text{C-P}} = 90.9$ Hz), 131.44 (d, $J_{\text{C-P}} = 2.7$ Hz), 130.40 (d, $J_{\text{C-P}} = 8.7$ Hz), 128.60 (d, $J_{\text{C-P}} = 11.0$ Hz), 29.66 (d, $J_{\text{C-P}} = 68.0$ Hz), 24.11 (d, $J_{\text{C-P}} = 14.5$ Hz), 23.50 (d, $J_{\text{C-P}} = 4.1$ Hz), 13.58. ^{31}P NMR (162 MHz CDCl$_3$): δ 40.83 ppm.

4.3.14. *Tert-butyldiphenylphosphine oxide (**3m**)*

[4h] Purification by chromatography (petroleum ether/EtOAc = 1:2) afforded **3m** (40.2 mg, 78%) as a white solid. R$_f$ = 0.60

(EtOAc); ^{1}H NMR (400 MHz CDCl$_3$): δ 7.96 (dd, $J = 8.4$ Hz, $J = 8.4$ Hz, 4H), 7.55–7.46 (m, 6H), 1.25 (d, $J = 14.8$ Hz, 9H). ^{13}C NMR (100 MHz CDCl$_3$): δ 132.20 (d, $J_{\text{C-P}} = 8.1$ Hz), 131.49 (d, $J_{\text{C-P}} = 2.7$ Hz), 131.17 (d, $J_{\text{C-P}} = 89.9$ Hz), 128.28 (d, $J_{\text{C-P}} = 10.9$ Hz), 33.97 (d, $J_{\text{C-P}} = 70.4$ Hz), 25.21. ^{31}P NMR (162 MHz CDCl$_3$): δ 38.77 ppm.

4.3.15. *Dicyclohexyl(phenyl)phosphine oxide (**3n**)*

[9] Purification by chromatography (petroleum ether/EtOAc = 1:2) afforded **3n** (32.5 mg, 56%) as a white solid. R$_f$ = 0.43 (EtOAc); ^{1}H NMR (400 MHz CDCl$_3$): δ 7.59 (dd, $J = 7.2$ Hz, $J = 7.2$ Hz, 2H), 7.42–7.40 (m, 3H), 1.98 (br, 4H), 1.75–1.53 (m, 8H), 1.24–1.05 (m, 10H). ^{13}C NMR (100 MHz CDCl$_3$): δ 131.46 (d, $J_{\text{C-P}} = 7.3$ Hz), 131.23 (d, $J_{\text{C-P}} = 0.6$ Hz), 129.84 (d, $J_{\text{C-P}} = 85.9$ Hz), 128.24 (d, $J_{\text{C-P}} = 10.1$ Hz), 35.10 (d, $J_{\text{C-P}} = 66.8$ Hz), 26.44 (d, $J_{\text{C-P}} = 11.6$ Hz), 26.33 (d, $J_{\text{C-P}} = 11.4$ Hz), 25.83, 25.49, 24.58 (d, $J_{\text{C-P}} = 2.0$ Hz). ^{31}P NMR (162 MHz CDCl$_3$): δ 45.43 ppm.

4.3.16. *Diisopropyl phenylphosphonate (**3o**)*

[4i] Purification by chromatography (petroleum ether/EtOAc = 2:1) afforded **3**° (33.9 mg, 70%) as a colorless oil. R$_f$ = 0.59 (petroleum ether/EtOAc = 1:1); ^{1}H NMR (400 MHz CDCl$_3$): δ 7.82 (dd, $J = 7.6$ Hz, $J = 13.2$ Hz, 2H), 7.53 (t, $J = 7.2$ Hz, 1H), 7.47–7.43 (m, 2H), 4.75–4.63 (m, 2H), 1.37 (d, $J = 6.0$ Hz, 6H), 1.23 (d, $J = 6.4$ Hz, 6H). ^{13}C NMR (100 MHz CDCl$_3$): δ 132.05 (d, $J_{\text{C-P}} = 2.9$ Hz), 131.65 (d, $J_{\text{C-P}} = 9.8$ Hz), 129.81 (d, $J_{\text{C-P}} = 188.6$ Hz), 128.28 (d, $J_{\text{C-P}} = 14.8$ Hz), 70.70 (d, $J_{\text{C-P}} = 5.5$ Hz), 24.02 (d, $J_{\text{C-P}} = 3.9$ Hz), 23.78 (d, $J_{\text{C-P}} = 4.7$ Hz). ^{31}P NMR (162 MHz CDCl$_3$): δ 16.64 ppm.

Notes

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.07.026.

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