Research Paper

Journal of Chemical Research

Nickel-catalyzed C–P cross-coupling of (het)aryl tosylates with secondary phosphine oxides

Journal of Chemical Research
1–7

DOI: 10.1177/1747519821994533
journals.sagepub.com/home/chl
SAGE

Xiao-Yun He

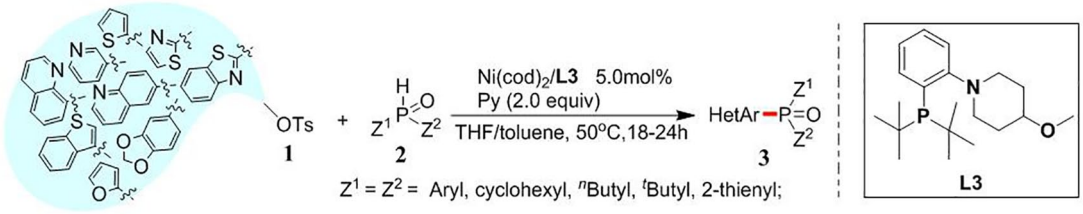
Abstract

A novel and convenient approach to the synthesis of various tertiary phosphine oxides via nickel-catalyzed cross-coupling of (het)aromatic tosylates with secondary phosphine oxides is developed. The reaction employs cheap nickel as the catalyst, 1-(2-(di-tert-butylphosphanyl)phenyl)-4-methoxypiperidine **(L3)** as the ligand, and pyridine as the base. This reaction produces the corresponding (het)aromatic phosphorus compounds in good to high yields. Moreover, four new tertiary phosphine oxides are reported in this process.

Keywords

C-P bond, (het)aromatic tosylates, nickel-catalyzed, phosphorylation, tertiary phosphine oxides

Date received: 23 December 2020; accepted: 25 January 2021



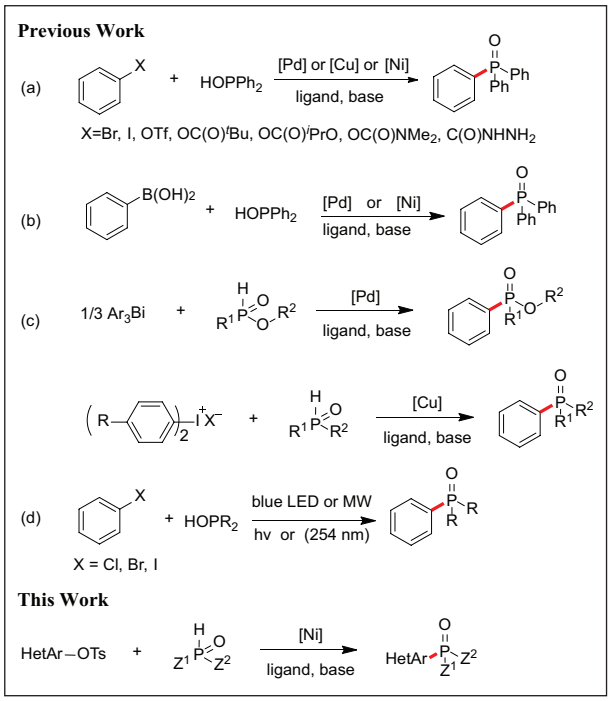
Introduction

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,[1,2] and their arylphosphine derivatives play an important role in organometallic catalysis[3,4] and organocatalysis.[5,6] Following on from the pioneering work of the Hirao group in this area,[7] after further development and modification, researchers have developed the palladium-, nickel-, and copper-catalyzed processes for the construction of C(sp)2-P bonds (Scheme 1, a).[8–10] Recently, oxidative phosphonylation of arylboronic acids catalyzed by palladium or nickel has become feasible (Scheme 1, b).[11,12] Diaryliodonium salts,[13] as important and valuable electrophilic arylation reagents, have attracted significant attention in recent years due to their high reactivity and nontoxicity and they have been found to serve as potential arylating agents for phosphorus nucleophiles (Scheme 1, c). The last two decades have witnessed the rapid development of bismuth chemistry. Organobismuth compounds are nontoxic and are easily available building blocks among the heavy nonradioactive main group elements.[14,15] Recently, Zhao and co-workers described the first examples of reactions of triarylbismuths with P(O)-H compounds under Pd(0) catalysis (Scheme 1, c).[16]

Furthermore, microwave-(MW) and visible-light-irradiated P-C coupling reactions have also been developed (Scheme 1, d).[17–19] To date, very few examples of nickel-catalyzed phosphinations of aryl mesylates and tosylates have been reported. In 2012, Zhang's group reported the first Ni-catalyzed P-arylation using aryl mesylates and tosylates as coupling partners in this field, greatly expanding the scope of transition-metal-catalyzed C-P couplings.[20] Yu's group has reported a novel phosphorylation of alkenyl and aryl C–O bonds via photoredox/nickel dual catalysis.[21] A variety of easily available and inexpensive sulfonates could be transformed into alkenyl phosphonates and aryl phosphine oxides

Department of Chemistry and Environmental Engineering, Hebei Chemical and Pharmaceutical College, Shijiazhuang, P.R. China

Corresponding author:
Xiao-Yun He, Department of Chemistry and Environmental Engineering, Hebei Chemical and Pharmaceutical College, Shijiazhuang 050026, P.R. China.
Email: 61027391@qq.com



Scheme 1. Methods for the synthesis of tertiary phosphine oxides.

with high selectivity and efficiency under mild reaction conditions. Very recently, Li reported the nickel-catalyzed phosphorylation of aryl tosylates; however, the use of an appropriate phosphine ligand was crucial for this reaction.[22] Ten significant ligands were then evaluated for their efficacy in this C–P bond coupling reaction, with the bidentate phosphine ligand 2-(di-*tert*-butylphosphino)-4-methoxyl-*N,N*-dimethylaniline **L1** proving to be the best candidate. On the basis of Li's developed system, we were interested in Ni-catalyzed coupling of 2-pyridyl tosylate **1a** with diphenylphosphine oxide **2a** as a model reaction system to optimize the catalytic conditions (Table 1).

Results and discussion

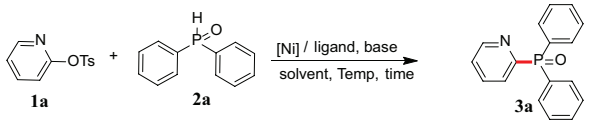
Initially, when **1a** (0.2 mmol) was added to a mixture of **2a** (0.3 mmol), $Ni(cod)_2$/**L1** (3.0 mol%), and N,N-Diisopropylethylamine (DIPEA) (1.5 equiv.) in Tetrahydrofuran (THF)/toluene (3:1) at 100 °C for 18 h under nitrogen, the desired P-arylation product **3a** was obtained in 48% yield (Table 1, entry 1). Encouraged by this result, we further examined the effect of the catalyst, the solvent, the ligand, the temperature, and the base on the reaction yield. Under similar reaction conditions, various Ni salts were examined, with $Ni(cod)_2$ being the most effective catalyst for the production of **3a** (Table 1, entries 1–4). In addition, the catalytic efficiency of various nickel complexes was evaluated (Table 1, entries 5–9). The results showed that among several nickel complexes, $NiCl_2$(dcype) was a potential catalyst, affording the desired product **3a** in 20% yield (Table 1, entry 8).

We, in Li's report, have described recently the application of L1 as a catalyst ligand for the cross-coupling of aryltosylate and dialkyl phosphite, despite the reactivity is modest in our system, L1 was shown to be among the most active ligands in their report. Encouraged by the catalytic abilities of L1, and the needs of our current research, we have designed several new ligands. Next, a subsequent screening of the role of different ligands to gain more insight and to find a more active and robust system was undertaken (Table 1, entries 1 and 10–17). Notably, in the course of these investigations, most of the ligands examined gave fairly poor results, with only bidentate ligand **L3** that was giving excellent results in promoting the reaction (Table 1, entry 11). The yield was slightly improved by increasing the molar amount of $Ni(cod)_2$/**L3** (Table 1, entry 18). Screening of different bases showed that pyridine (Py) was the most suitable base for this procedure, giving **3a** in 75% yield (Table 1, entries 18–25). Investigation of different solvents in this transformation was carried out and the results indicated that the solvent plays a crucial role in this reaction system. THF/toluene (3:1) gave the best yield of 85% (Table 1, entries 26–30). Increasing the amount of Py gave a slightly better yield (Table 1, entry 31) and prolonging the reaction time further increased the yield to 93% under otherwise identical conditions (Table 1, entry 32).

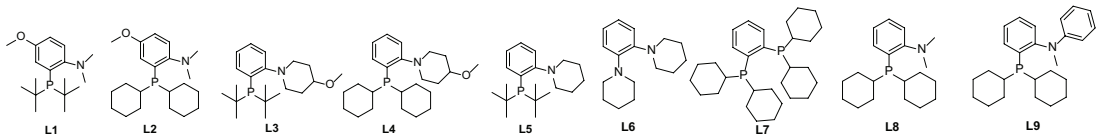
Thus, the optimized experimental conditions are as follows: $Ni(cod)_2$/**L3** (5.0 mol%), Py (2.0 equiv.) as the base in THF/toluene (v/v: 3:1) at 50 °C. The scope of this method was extended to the reaction of a wide range of (het)aryl tosylates with different secondary phosphine oxides. As shown in Table 2, different secondary phosphine oxides were all efficiently coupled under these reaction conditions to provide the corresponding P-(het)arylated derivatives with good to excellent isolated yields, showing that this protocol is a general and practical method for the preparation of various valuable symmetric or nonsymmetric tertiary phosphines oxides. The scope of the substrates was mainly examined by varying the N-heteroaromatic tosylate compounds, which are key to many metal-catalyzed organic transformations.[23,24] First, eight (het)aryl tosylates were coupled with $Ph_2P(O)H$ **2a** to produce the corresponding products in good to high yields. High yields were obtained with both electron-rich and electron-deficient (het)aryl tosylates (Table 2, entries 1–7). The reaction was inefficient under the current reaction conditions from sesamol derivatives, reaction with **2a** gave the desired product **3i** in only 35% yield (Table 2, entry 8). In addition to diphenylphosphine oxide, when the aromatic group was substituted with other groups, secondary phosphine oxides with electron-donating groups or electron-withdrawing groups reacted smoothly with hydroxybenzothiazolyl tosylates to provide the desired products in excellent yields (Table 2, entries 11 and 12).

However, secondary phosphine oxides with strong electron-withdrawing groups, such as fluoro, resulted in a lower yield. These results indicate that the yields were dependent primarily on the electronic properties of the secondary phosphine oxides (Table 2, entry 11). Secondary phosphine oxides with sterically demanding *o*-substituted aromatic rings afforded inferior yields, illustrating that steric hindrance has an influence on this coupling reaction (Table 2, entry 9).

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



Entry	[Ni]/ligand[b]	Base	Solvent	Yield[c]	Entry	[Ni]/ligand	Base	Solvent	Yield (%)[c]
1[d]	$Ni(cod)_2$/**L1**	DIPEA	Toluene	48	17[d]	$Ni(cod)_2$/**L9**	DIPEA	Toluene	38
2[d]	$Ni(OAc)_2.4H_2O$/**L1**	DIPEA	Toluene	Trace	18	$Ni(cod)_2$/**L3**	DIPEA	Toluene	69
3[d]	$Ni(acac)_2$/**L1**	DIPEA	Toluene	43	19	$Ni(cod)_2$/**L3**	TMEDA	Toluene	45
4[d,e]	$NiCl_2$/**L1**	DIPEA	Toluene	n.r.	20	$Ni(cod)_2$/**L3**	*t*-BuOLi	Toluene	11
5[d,e]	$NiCl_2(PCy_3)_2$	DIPEA	Toluene	n.r.	21	$Ni(cod)_2$/**L3**	*t*-BuOK	Toluene	9
6[d]	$NiCl_2$(dppe)	DIPEA	Toluene	Trace	22	$Ni(cod)_2$/**L3**	K_2CO_3	Toluene	18
7[d,e]	$NiCl_2(PPh_3)_2$	DIPEA	Toluene	n.r.	23	$Ni(cod)_2$/**L3**	K_3PO_4	Toluene	15
8[d]	$NiCl_2$(dcype)	DIPEA	Toluene	20	24	$Ni(cod)_2$/**L3**	Py	Toluene	75
9[d]	$NiCl_2$(dppf)	DIPEA	Toluene	8	25[e,f]	$Ni(cod)_2$/**L3**	–	Toluene	n.r.
10[d]	$Ni(cod)_2$/**L2**	DIPEA	Toluene	51	26	$Ni(cod)_2$/**L3**	Py	Dioxane	53
11[d]	$Ni(cod)_2$/**L3**	DIPEA	Toluene	62	27[e]	$Ni(cod)_2$/**L3**	Py	Acetonitrile	n.r.
12[d]	$Ni(cod)_2$/**L4**	DIPEA	Toluene	45	28[b]	$Ni(cod)_2$/**L3**	Py	THF	78
13[d]	$Ni(cod)_2$/**L5**	DIPEA	Toluene	5	29[g]	$Ni(cod)_2$/**L3**	Py	THF	80
14[d]	$Ni(cod)_2$/**L6**	DIPEA	Toluene	31	30	$Ni(cod)_2$/**L3**	Py	THF/toluene (v/v: 3:1)	85
15[d]	$Ni(cod)_2$/**L7**	DIPEA	Toluene	12	31[h]	$Ni(cod)_2$/**L3**	Py	THF/toluene (v/v: 3:1)	89
16[d]	$Ni(cod)_2$/**L8**	DIPEA	Toluene	40	32[i]	$Ni(cod)_2$/**L3**	Py	THF/toluene (v/v: 3:1)	93



[a]Unless otherwise stated, the reaction conditions are as follows: Heteroaromatic tosylate **(1a)** (0.2 mmol), diphenyl phosphite **(2a)** (0.3 mmol), [Ni]/ligand (5.0 mol%), base (1.5 equiv.), solvent (2 mL), reaction time was 12 h, N_2.
[b]Stirred at 80 °C.
[c]Yield of isolated product.
[d][Ni]/ligand (3.0%).
[e]No reaction.
[f]No base was used.
[g]Stirred at 50 °C.
[h]Py (2.0 equiv.).
[i]Py (2.0 equiv.), reaction time was 18 h.

We also tested our cross-coupling procedure for the assembly of a bis(heterocyclic) product. A 2-hydroxybenzothiazolyl tosylate readily underwent coupling with dithiophenylphosphine oxide to provide a bis(heterocyclic) compound (Table 2, entry 13). Other hydrogen phosphoryl compounds were also applicable in this transformation. In addition to diarylphosphine oxides **2a–f**, aliphatic *n*-$Bu_2P(O)H$ (Table 2, entry 14), the $Cy_2P(O)H$ (Table 2, entries 15–17), and bulky *t*-$Bu_2P(O)H$ (Table 2, entries 18–22) coupled with (het)aryl tosylates readily by increasing the equivalent of base, producing the corresponding products in moderate to high yields.

Conclusion

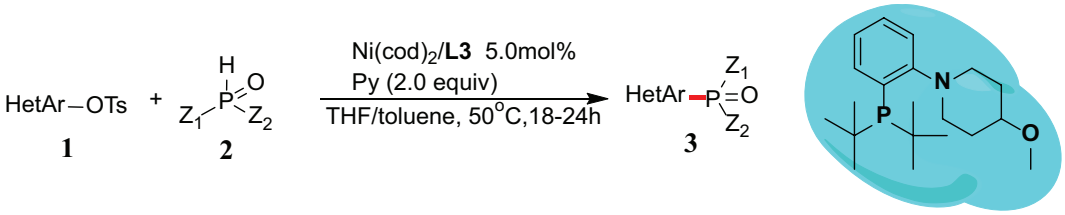
In summary, we have developed a novel nickel-catalyzed carbon-phosphine cross-coupling protocol from a wide range of (het)aromatic tosylates and different secondary phosphine oxides. Notably, the process is simple and proceeds under mild reaction conditions. Moreover, the process is generally cheaper overall because more accessible (het)aryl phenol derivatives are used to form the C-P bond. These advantages should help this C-P bond-forming method to find broad application in both complex molecule synthesis and for the preparation of P-chiral organophosphorus compounds.

Experimental

General

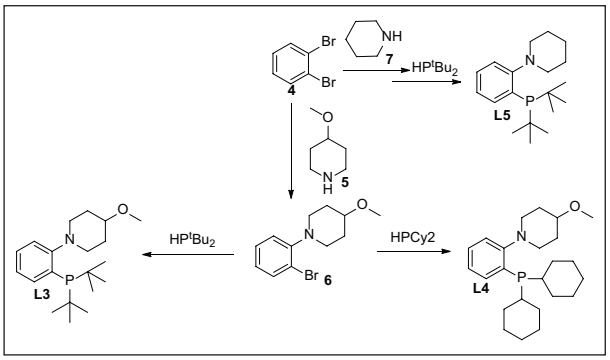
$Ni(cod)_2$ (98%), $Ni(acac)_2$ (>98%), $NiCl_2(PCy_3)_2$ (>98%), $NiCl_2$(dppe) (98%), $NiCl_2$(dcype) (>98%), $NiCl_2$(dppf) (99%), $NiCl_2(PPh_3)_2$ (>98%), Pd_2dba_3, $Pd(OAc)_2$, and DiPPF were purchased from Aldrich. $Ni(OAc)_2{\cdot}4H_2O$, $NiCl_2$, racemic-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), and Tetramethylethylenediamine (TMEDA) (⩾99%) were purchased from Alfa Aesar. Other reagents were available commercially and were used without further purification, unless otherwise indicated. All aryl tosylates were prepared according to the literature procedures.[25–29] Ligands **L1**, **L2**, **L6**, **L7**, **L8**, and **L9** were prepared

Table 2. Cross-coupling of various heteroaromatic tosylates with disubstituted phosphine oxide.[a]



Entry	Substrate 1	Substrate 2	Product	Yield[b] (%)	Entry	Substrate 1	Substrate 2	Product	Yield[b] (%)
1	**1b**	**2a**	**3b**	83	12	**1j**	**2e**	**3m**	87
2	**1c**	**2a**	**3c**	92	13	**1j**	**2f**	**3n**	72
3	**1d**	**2a**	**3d**	83	14	**1j**	**2g**	**3o**[c]	73
4	**1e**	2a	**3e**	86	15	**1j**	**2h**	**3p**[c]	78
5	**1f**	**2a**	**3f**	85	16	**1f**	**2h**	**3q**[c]	75
6	**1g**	**2a**	**3g**	88	17	**1a**	**2h**	**3r**[c]	71
7	**1h**	**2a**	**3h**	89	18	**1a**	**2i**	**3s**[c]	70
8	**1i**	**2a**	**3i**	35	19	**1b**	**2i**	**3t**[c]	75
9	**1j**	**2b**	**3j**	77	20	**1c**	**2i**	**3u**[c]	74
10	**1j**	**2c**	**3k**	88	21	**1d**	**2i**	**3v**[c]	76
11	**1j**	**2d**	**3l**	56	22	**1e**	**2i**	**3w**[c]	73

[a]Reaction conditions: heteroaromatic tosylate **(1a)** (0.2 mmol), diphenyl phosphite **(2)** (0.3 mmol), Ni(cod)$_2$/**L2** (5.0 mol%), Py (2.0 equiv.), THF/toluene (v/v: 3/1) (2 mL), N_2, at 50 °C for 18–24 h.
[b]Yield of the isolated product.
[c]Py (3.5 equiv.).



Scheme 2. Synthesis of ligands **L3**, **L4**, and **L5.**

according to literature procedures.[22,30–33] Reactions were run under an argon atmosphere with exclusion of moisture from reagents and glassware using standard Schlenk techniques. Solvents were dried from molecular sieves and kept under argon. Spectroscopic data of known compounds matched with the data reported in the corresponding references.[34–42] All new compounds were further characterized by high-resolution mass spectrometry (HRMS) (EI), elemental analysis, and ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. High-resolution mass spectra were obtained using a GCT time of flight (TOF) instrument with the electron ionization (EI) source. Elemental analyses were performed with the German elemental analyzer Vario EL. NMR measured on Bruker 400M spectrometers. ^{1}H NMR and ^{13}C NMR were recorded using tetramethylsilane (TMS) as the internal standard and 85% H_3PO_4 as the external standard for ^{31}P NMR spectra. Chemical shifts are reported in parts per million (δ). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; and m, multiplet. The coupling constants, *J*, are reported in Hertz (Hz). The products were purified by column chromatography on aladdin silica gel (300–400 mesh) under an argon atmosphere.

Experimental section

General procedure A: ligand synthesis and characterization. A Schlenk tube was charged with reagents: Pd_2dba_3 (46 mg, 5 mol% Pd), BINAP (93 mg, 7.5 mol%), NaO^{t}Bu (231 mg, 2.4 mmol, 1.2 equiv.), 1,2-dibromobenzene **(4)** (2.0 mmol), and 4-methoxypiperidine **(5)** (2.0 mmol, 1.0 equiv.). Toluene (5 mL) and a stir bar were added. Then, the mixture was then stirred in an oil bath at 80 °C for 15 h under Ar. Upon completion, the mixture was concentrated and the residue was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired product **(6)** in 71% yield.

To a Schlenk tube, $Pd(OAc)_2$ (typically 3 mol%) and DiPPF [1,1′-bis(diisopropylphosphino)ferrocene; Pd:L = 1:1.2], di(cyclohexyl)phosphine (1.2 mmol), and NaO^{t}Bu (1.44 mmol) were added, followed by the aryl halide **6** (1.2 mmol) in toluene (6 mL). The Schlenk tube was then degassed twice. The resulting mixture was heated at 110 °C until complete consumption of the phosphine was achieved. The solution was then cooled and filtered through a plug of silica, which in turn was washed with CH_2Cl_2. Removal of the solvent from the combined eluent afforded the Ligand **L4** in 63% yield that was further purified by recrystallization or by washing with appropriate solvents. All ligands were worked up in air and were found to be stable when handled on the bench top. Ligand **L3** was prepared by the coupling of (^{t}butyl)$_2$PH and 1-(2-bromophenyl)-4-methoxypiperidine, via the standard procedure employing 3 mol% Pd and 3.6 mol% ligand DiPPF in 57% yield as a white solid (Scheme 2).

*1-(2-(di-*tert*-butylphosphanyl)phenyl)-4-methoxypiperidine* (**L3**): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.55 (m, 1H), 7.30–7.21 (m, 1H), 7.10–7.04 (m, 2H), 3.34 (s, 3H), 3.32–3.26 (m, 1H), 3.24–3.18 (m, 2H), 2.88–2.79 (m, 2H), 2.05–1.97 (m, 2H), 1.94–1.83 (m, 2H), 1.24 (d, J = 14.8 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2 (d, J_{PC} = 17.2 Hz), 136.5, 133.7 (d, J_{PC} = 18.6 Hz), 130.6, 123.4, 121.2, 75.2, 55.3, 44.7, 44.6, 33.8 (d, J = 24 Hz), 30.8 (d, J = 14.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ −26.4.

(HRMS) (EI): m/z [M]$^+$ calcd for $C_{20}H_{34}NOP$: 335.2378; found: 335.2373. Anal. calcd for $C_{20}H_{34}NOP$: C, 71.61; H, 10.22; N, 4.18; found: C, 71.73; H, 10.29; N, 4.31.

1-(2-Dicyclohexylphosphinophenyl)-4-methoxypiperidine **(L4):** Colorless oil, yield 63%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.53 (m, 1H), 7.30–7.20 (m, 1H), 7.11–7.03 (m, 2H),3.35 (s, 3H), 3.32–3.26 (m, 1H), 3.24–3.21 (m, 2H), 2.86–2.81 (m, 2H), 2.01–1.94 (m, 8H), 1.77–1.63 (m, 8H), 1.33–0.95 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3 (d, J_{PC} = 17.2 Hz), 133.2, 132.0 (d, J_{PC} = 18.0 Hz), 129.3, 123.6, 120.9, 75.0, 55.2, 44.7, 44.6, 35.3 (J = 13.0 Hz), 31.2 (J = 20.4 Hz), 29.8 (J = 8.8 Hz), 27.4, 27.2 (J = 4.8 Hz), 26.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ −23.5.

(HRMS) (EI): m/z [M]$^+$ calcd for $C_{24}H_{38}NOP$: 387.2691; found: 387.2687. Anal. calcd for $C_{24}H_{38}NOP$: C, 74.38; H, 9.88; N, 3.61; found: C, 74.43; H, 9.93; N, 3.72.

*1-(2-(di-*tert*-butylphosphanyl)phenyl)piperidine* (**L5**): Colorless oil, yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.54 (m, 1H), 7.32–7.23 (m, 1H), 7.12–7.00 (m, 2H), 2.75–2.73 (m, 4H), 1.37–1.32 (m, 6H), 1.25 (d, J = 14.2 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9 (d, J_{PC} = 17.0 Hz), 136.3, 133.6 (d, J_{PC} = 18.2 Hz), 130.4, 123.1, 121.0, 54.3, 33.7 (d, J = 23.6 Hz), 30.8 (d, J = 15.0 Hz), 26.6, 24.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ −22.3.

(HRMS) (EI): m/z [M]$^+$ calcd for $C_{19}H_{32}NP$: 305.2272; found: 305.2276. Anal. calcd for $C_{19}H_{32}NP$: C, 74.71; H, 10.56; N, 4.59; found: C, 74.75; H, 10.59; N, 4.62.

General procedure B: phosphination of (Het)aromatic tosylates with secondary phosphine oxides

In an argon-filled glovebox, an oven-dried Schlenk tube equipped with a Teflon stir bar was charged with $Ni(cod)_2$/**L3** (5 mol%) followed by anhydrous THF (1.0 mL), secondary phosphine oxide **(2)** (0.3 mmol), and Py (2.0 equiv.). The solution was stirred for 5–10 min. Next, the (het)aromatic tosylate **(1)** (0.2 mmol) was added at once followed by anhydrous toluene/THF (0.5 mL/0.5 mL). The Schlenk tube was sealed with a Teflon valve and

the reaction mixture was stirred at 50 °C for 18–24 h. The reaction mixture was then cooled to room temperature, filtered, and rinsed with dichloromethane to remove any insoluble residues. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to give the analytically pure product. All products prepared using this synthetic method (**3a**, **3b**, **3c**, **3d**, **3e**, **3f, 3g, 3h, 3i, 3j, 3k, 3l, 3m, 3n, 3o, 3p, 3q, 3r, 3s)** have been reported earlier, and their spectral data matched with those presented in the literature. Products **3t, 3u, 3v,** and **3w** are novel compounds.

di-tert-*butyl(pyridin-3-yl)phosphine oxide* **(3t):** Colorless oil, yield 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65–8.61 (m, 2H, H pyridine), 8.02–7.98 (m, 1H, H pyridine), 7.41–7.37 (m, 1H, H pyridine), 1.23 (d, J = 13.0 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 152.0 (d, J = 12.2 Hz), 139.2 (d, J = 7.8 Hz), 132.0, 131.2 (d, J = 106.2 Hz), 35.7 (d, J = 75.1 Hz), 34.9 (d, J = 74.9 Hz), 27.0, 26.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ 48.7. (HRMS) (EI): m/z $[M]^+$ calcd for $C_{13}H_{22}NOP$: 239.1439; found: 239.1436. Anal. calcd for $C_{13}H_{22}NOP$: C, 65.25; H, 9.27; N, 5.85; found: C, 65.35; H, 9.31; N, 5.90.

di-tert-*butyl(thiophen-2-yl)phosphine oxide* **(3u):** Colorless oil; yield 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.65 (m, 1H, H thiophene), 7.51–7.46 (m, 1H, H thiophene), 7.22–7.17 (m, 1H, H thiophene), 1.22 (d, J = 13.2 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.7 (d, J = 8.1 Hz), 132.6 (d, J = 4.2 Hz), 132.8 (d, J = 102.1 Hz), 128.8 (d, J = 12.0 Hz), 35.8 (d, J = 75.6 Hz), 35.1 (d, J = 75.3 Hz), 27.2, 26.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 46.6.

(HRMS) (EI): m/z $[M]^+$ calcd for $C_{12}H_{21}OPS$: 244.1051; found: 244.1046. Anal. calcd for $C_{12}H_{21}OPS$: C, 58.99; H, 8.66; S, 13.12; found: C, 59.01; H, 8.71; S, 13.16.

di-tert-*butyl(quinolin-8-yl)phosphine oxide* **(3v):** Yellow oil; yield 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82–8.75 (m, 1H, H quinoline), 8.39 (dd, 1H, J = 14.0, J = 7.2 Hz, H quinoline), 8.23 (d, 1H, J = 8.1 Hz, H quinoline), 8.08 (d, 1H, J = 7.2, H quinoline), 7.73–7.68 (m, 1H, H quinoline), 7.46–7.41 (m, 1H, H quinoline), 1.24 (d, J = 12.8 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 149.5 (d, J = 4.4 Hz), 138.1 (d, J = 7.2 Hz), 136.3, 133.9 (d, J = 109.4 Hz), 133.5, 132.3, 128.7 (d, J = 11.2 Hz), 121.8, 36.3 (d, J = 77.1 Hz), 35.8 (d, J = 76.9 Hz), 27.8, 26.9. ^{31}P NMR (162 MHz, $CDCl_3$): δ 36.9.

(HRMS) (EI): m/z $[M]^+$ calcd for $C_{17}H_{24}NOP$: 289.1596; found: 289.1593. Anal. calcd for $C_{17}H_{24}NOP$: C, 70.57; H, 8.36; N, 4.84; found: C, 70.63; H, 8.41; N, 4.89.

di-tert-*butyl(quinolin-6-yl)phosphine oxide* **(3w):** Yellow oil; yield 73%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.05 (s, 1H), 8.40–8.37 (m, 1H, H quinoline), 8.25–8.22 (m, 1H, H quinoline), 8.20–8.17 (m, 1H, H quinoline), 7.88–7.84 (m,1H, H quinoline), 7.55–7.51 (m, 1H, H quinoline), 1.23 (d, J = 12.6 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 149.3, 137.1, 134.3 (d, J = 9.2 Hz), 132.3, 132.2 (d, J = 105.6 Hz), 130.8 (d, J = 11.0 Hz), 129.9 (d, J = 11.2 Hz), 122.4, 36.1 (d, J = 76.2 Hz), 35.4 (d, J = 75.6 Hz), 27.4, 26.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 37.8.

(HRMS) (EI): m/z $[M]^+$ calcd for $C_{17}H_{24}NOP$: 289.1596; found: 289.1591. Anal. calcd for $C_{17}H_{24}NOP$: C, 70.57; H, 8.36; N, 4.84; found: C, 70.64; H, 8.43; N, 4.88.

Acknowledgements

The author is thankful to Hebei University of Science and Technology for ^{13}C NMR, ^{1}H NMR, ^{31}P NMR, HRMS(EI), and elemental analysis.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: The author gratefully acknowledges the financial support from Hebei Chemical and Pharmaceutical College and the Higher Education Scientific Research Project of Hebei Province (2020) (SQ201044).

ORCID iD

Xiao-Yun He https://orcid.org/0000-0002-4540-9788

Supplemental material

Supplemental material for this article is available online.

References

1. Yoshino K, Kohno T, Tsukamoto G, et al. *J Med Chem* 1989; 32: 1528.
2. Hérault D, Nuel D, Buono G, et al. *Chem Soc Rev* 2015; 44: 2508.
3. McCarthy M and Guiry PJ. *Tetrahedron* 2001; 57: 3809.
4. Surry DS and Buchwald SL. *Chem Sci* 2011; 2: 27.
5. Lu X, Zhang C and Xu Z. *Acc Chem Res* 2001; 34: 535.
6. Wei Y and Shi M. *Acc Chem Res* 2010; 43: 1005.
7. Hirao T, Masunaga T, Ohshiro Y, et al. *Bull Chem Soc Jpn* 1982; 55: 909.
8. Rao HH, Jin Y, Zhao YF, et al. *Chem Eur J* 2006; 12: 3636.
9. Huang J, Liu Z, Zhang B, et al. *Inorg Chem* 2019; 58: 4253.
10. Dong JY, Liu L, Han LB, et al. *Org Lett* 2019; 21: 3198.
11. Fu TT, Qiao HW, Zhao YF, et al. *Org Biomol Chem* 2014; 18: 2895.
12. Hu GB, Chen WZ, Zhao YF, et al. *Org Lett* 2013; 15: 5362.
13. Xu J, Zhang PB, Zhao YF, et al. *J Org Chem* 2013; 78: 8176.
14. Suzuki H and Matano Y. *Organo-bismuth chemistry*. Amsterdam: Elsevier, 2001.
15. Maeda S and Patai S. *In the chemistry of organic arsenic, antimony and bismuth compounds*. New York: Wiley, 1994, p. 725.
16. Wang T, Sang S, Zhao YF, et al. *J Org Chem* 2014; 79: 608.
17. Zeng HY, Dou Q and Li CJ. *Org Lett* 2019; 21: 1301.
18. Ananthnag GS, Mague JT and Balakrishna MS. *Dalton Trans* 2015; 44: 3785.
19. Zhu DL, Jiang S, Li HX, et al. *Org Lett* 2021; 23: 160.
20. Shen CR, Yang GQ and Zhang WB. *Org Biomol Chem* 2012; 10: 3500.
21. Liao LL, Gui YY and Yu DG. *Org Lett* 2017; 19: 3735.
22. Li CJ. *Russ Gen Chem* 2020; 90: 725.
23. Minnaard AJ, Feringa BL, Vries JG, et al. *Acc Chem Res* 2007; 40: 1267.
24. Diederich F and Stang PJ. *Metal-catalyzed cross-coupling reactions*. Weinheim: Wiley-VCH Verlag GmbH, 1998.
25. Yang JF, Zheng JF, Zhou JR, et al. *Eur J Med Chem* 2012; 31: 6248.
26. Lei XY, Stafford JM, Cao B, et al. *Synthesis* 2015; 47: 2578.

27. Kwong FY, Lee HW, So CM, et al. *Org Chem Front* 2020; 7: 926.
28. Langille NF, Dakin LA, Panek JS, et al. *Org Lett* 2002; 4: 2485.
29. Belley M, Douida Z, Mancuso J, et al. *Synlett* 2005; 2: 247.
30. Cheng K, Zeng MF, Qi CZ, et al. *J Med Chem* 2013; 37: 99.
31. Harada T, Ueda Y, Sawamura M, et al. *Chem Commun* 2018; 54: 1718.
32. Bedford RB, Brenner PB, Carter E, et al. *Organometallics* 2014; 33: 5767.
33. Li PB, Fu CL, Ma SM, et al. *Adv Synth Catal* 2013; 35: 1255.
34. Yun J, To WP, Che CM, et al. *Org Lett* 2018; 20: 7816.
35. Zhang HY, Sun M, Yang SD, et al. *Org Biomol Chem* 2012; 10: 9627.
36. Yang J, Chen TQ and Han LB. *J Am Chem Soc* 2015; 137: 1782.
37. Isshiki R, Muto K and Yamaguchi J. *Org Lett* 2018; 20: 1150.
38. Luo K, Chen YZ, Wu L, et al. *Org Lett* 2016; 18: 452.
39. Li L, Wang JJ, Wang GW, et al. *J Org Chem* 2016; 81: 5433.
40. Peng P, Peng L, Lei AW, et al. *Org Chem Front* 2016; 6: 749.
41. Stankevič M and Włodarczyk A. *Tetrahedron* 2013; 69: 73.
42. Gowrisankar S, Neumann H, Beller M, et al. *Chem Eur J* 2013; 19: 15979.