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Palladium-catalyzed phosphination of functionalized aryl triflates

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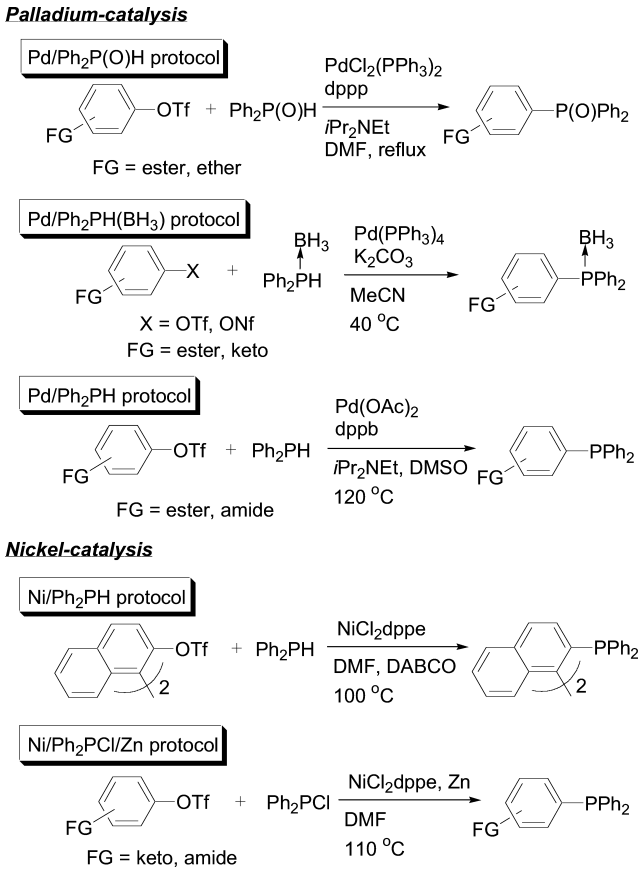
Abstract—Catalytic user-friendly approach to the syntheses of various functionalized aromatic phosphines from their corresponding substituted aryl triflates and triarylphosphines was accomplished. This method is carried out in neutral media and compatible with many functional groups including aldehyde, keto, ester, nitrile, ether and pyridyl groups.

1. Introduction

Functionalized aromatic phosphines are an important type of ligands in transition metal-catalyzed reactions.[1,2] However, the synthesis of substituted tertiary phosphines by Grignard/organolithium reagents is limited to aryl bromides/iodides and is not applicable to triflate substrates.[3] As phenols and their derivatives are easily accessible, it is valuable to develop a transition metal-catalyzed phosphination of functionalized aryl triflates. Several palladium- and nickel-catalyzed phosphination of aryl sulfonates have been reported (Scheme 1). The Pd/$Ph_2P(O)H$ protocol for phosphinylation of aryl triflates using diphenylphosphine oxide as the phosphinylating agent was found to be compatible with some functional groups such as ester and ether groups (Scheme 1).[4] Nevertheless, this reaction could not be applied to the synthesis of BINAPO since only one triflate moiety (from BINOL ditriflates) was found to undergo phosphinylation as reported by Morgan et al.[5] Moreover, Bringmann, also demonstrated the failed transformation of 2,6-disubstituted aryl triflates to diphenylphosphine oxide group by palladium-catalyzed phosphinylation.[6] Using the above phosphinylation, the desired aromatic phosphine products usually were accomplished with a subsequent reduction of phosphine oxide intermediate with trichlorosilane, which is a disadvantage of this methodology. Recently, Lipshutz and co-workers reported palladium-mediated couplings of aryl nonaflates and triflates with diphenylphosphine–borane ($Ph_2PH–BH_3$) in the preparation of broane-stabilized unsymmetrical arylphosphines (Scheme 1).[7] The diphenylphosphine–borane is an air-stable reagent and readily prepared from commercially available Ph_2PCl and BH_3–THF in the presence of lithium aluminum hydride.[8] This method offers a low temperature advantage, but is sensitive to amine and pyridine groups, and further deprotection of borane group



Scheme 1. Transition metal-catalyzed phosphination of aryl triflates.

Keywords: phosphination; aryl triflates; triphenylphosphine.
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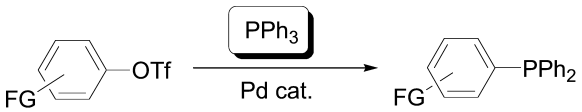
is required by using diethylamine to yield free phosphines.[9] The use of Ph_2PH protocol catalyzed by palladium complexes was applicable to aryl triflates (thyrosine and glycine derivatives) in DMSO solvent (Scheme 1).[10]

Apart from the palladium complexes, nickel catalysts were used in the transition metal-catalyzed phosphination. Cai et al. reported the first example of $NiCl_2$(dppe) catalyzed phosphination of BINOL ditriflate using diphenylphosphine (Ph_2PH) in the synthesis of BINAP (Scheme 1).[11] This direct nickel-catalyzed phosphination was found to be effective in the synthesis of diphosphines from ditriflates which failed in the Pd/$Ph_2P(O)H$ methodology previously.[5] Most importantly, these reaction conditions were amenable to the synthesis of optically active BINAPs from their optically active BINOL ditriflates. The minor drawbacks of this reaction are the use of air- and moisture-sensitive diphenylphosphine reagents and the requirement of portion-wise addition of Ar_2PH during the course of reaction. Recently, Ager and co-workers had used chlorodiphenyl-phosphine (Ph_2PCl) instead of diphenylphosphine as the phosphinating reagent (Scheme 1).[12] Zinc performs two functions in the Ni/Ph_2PCl/Zn protocol; it reduces Ni(II) to Ni(0) and presumably gives rise to zinc phosphide Ph_2-PZnCl which reacts with aryl triflates (Scheme 1). Although air-sensitive reagent is required, this method is mild. Synthesis of optically active BINAP without racemization is accomplished.[12]

We have recently described that triarylphosphines could be used as the diarylphosphinating agents for the preparation of substituted phosphines from the corresponding aryl bromides.[13] As phenols and their sulfonate derivatives are easily accessible, herein we report an alternative user-friendly and operationally simple palladium-catalyzed phosphination of functionalized aryl triflates using air-stable and economical triarylphosphines as the diarylphosphinating agents (Eq. (1)).[14]



(1)

FG = CHO, C(O)Me, COOMe, CN, OMe, py

2. Results and discussions

4-Acetylphenyltriflate (**1**) was used as the prototypical substrate for screening optimal reaction conditions. Both $Pd(PPh_3)_4$ and $Pd(OAc)_2$ were found to be effective catalysts.[15] $Pd(OAc)_2$ was preferred since other triaryl-phosphines can be used as the phosphinating agents.[15] Polar aprotic solvents were found to be effective and DMF was the solvent of choice.[15] The amount of triphenylphosphine agent added was found to be crucial in the phosphination of aryl triflates. The optimal amount of triphenylphosphine used was found to be about 2.3–2.5 equiv. (Fig. 1).

Thus, the optimal reaction conditions for the transformation of 4-acetylphenyltriflate (**1**) to 4-(diphenylphosphino)aceto-phenone (**2**) were found to require 10 mol% $Pd(OAc)_2$ and

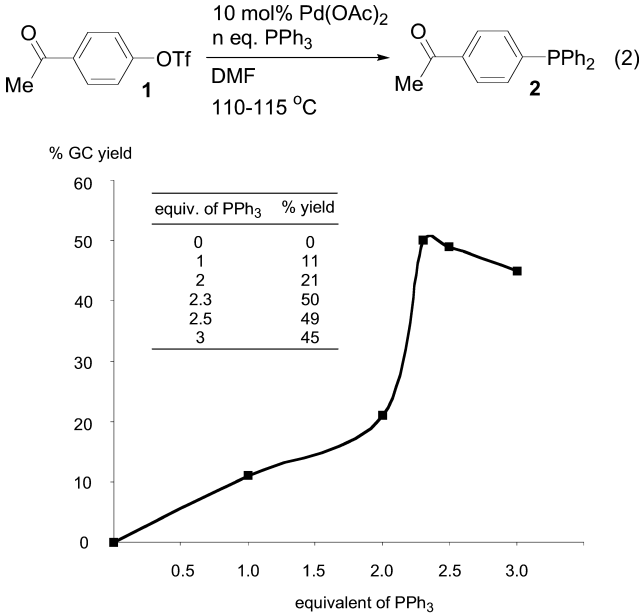


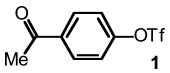
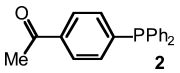
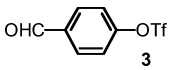
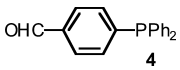
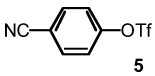
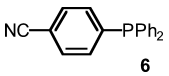
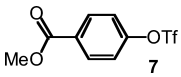
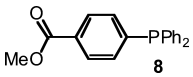
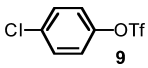
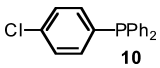
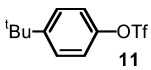
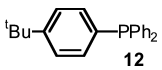
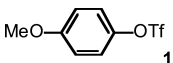
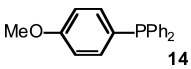
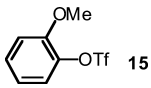
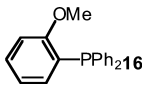
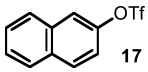
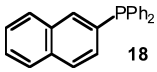
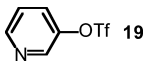
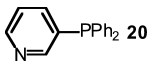
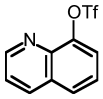
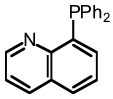
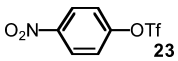
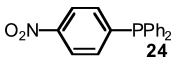
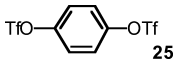
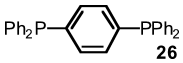
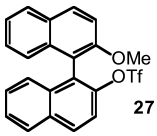
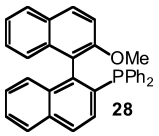
Figure 1. Effect of triphenylphosphine on the phosphination of aryl triflate.

2.3 equiv. of Ph_3P in DMF at 110–115°C under a nitrogen atmosphere. These reaction conditions were then applied to the syntheses of other functionalized aryl phosphines. 4-Formylphenyl triflate was directly phosphinated by triphenylphosphine to form 4-(diphenylphosphino)benzal-dehyde (Table 1, entry 2). In contrast, the previous preparation of this phosphine, which finds many appli-cations in water-soluble polymers[16] and porphyrins,[17] involved a muti-step synthesis requiring protection/depro-tection of the aldehyde group.[18] Other functional groups, such as ester, nitrile, keto, ether and chloride were tolerated with this phosphination reaction (Table 1, entries 2–7). However, previous syntheses of ester and nitrile containing phosphines required a long synthetic pathway.[19] A sterically hindered substrate, 2-methoxyphenyl triflate successfully reacted with Ph_3P to give 2-(diphenylphosphino)anisole (Table 1, entry 8). In contrast, the analogous less reactive 2-bromoanisole did not react. The transformation of quinolyl and pyridyl triflates to their corresponding phosphines required much longer reaction times (Table 1, entries 10–11). Presumably the chelating heteroatom coordinated to the palladium center rendered the complex coordinatively saturated.[20] Hence the catalytic activity was reduced. The quinolyl phosphine (entry 11) is a useful bidentate *P*,*N* ligand.[21]

Although this palladium-catalyzed phosphination tolerated many functional groups, it was incompatible with nitro group (Table 1, entry 12) which was reduced. The preparation of diphosphines from ditriflates was unsuccess-ful (Table 1, entry 13). Presumably, the inhibition is due to the inhibiting effect of excess phosphine (Table 1, entry 13 and Fig. 1). Extremely sterically hindered MOP precursor was found to be inferior in the reaction conditions (Table 1, entry 14). No significant electronic effects were observed in these phosphination reactions.

Other triarylphoshphines were found to be effective diarylphosphinating agents for palladium catalyzed phos-phination of aryl triflates (Table 2). The 4-acetophenyl

Table 1. Palladium-catalyzed phosphination of aryl triflates[a]

Entry	Substrates	Products	Time (h)	Percentage yield[b]
1	 1	 2	2	37
2	 3	 4	3	31
3	 5	 6	3	38
4	 7	 8	5	30
5	 9	 10	5	45[c]
6	 11	 12	6	50[c]
7	 13	 14	6	20 (25)[c]
8	 15	 16	8	28
9	 17	 18	4	51[c]
10	 19	 20	24	20 (33)[c]
11	 21	 22	72	45
12	 23	 24	48	Nil[d]
13	 25	 26	96	Nil[d]
14	 27	 28	120	Nil[e]

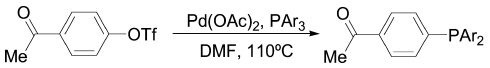
[a] Reaction conditions: ArOTf (0.5 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (1.15 mmol) and dry DMF (2 mL) were heated to 110–115°C under nitrogen.
[b] Isolated yields were reported.
[c] GC yields were reported.
[d] Starting material was consumed within 24 h.
[e] Starting material remained.

triflate was diarylphosphinated by tri(*m*-xylyl)phosphine, tri(*p*-methoxyphenyl)phosphine and tri(*p*-tolyl)phosphine to yield the corresponding aromatic phosphines in moderate yields with similar reaction rates (Table 2, entries 1–3). Sterically hindered tri(*o*-tolyl)phosphine did not react at all (Table 2, entry 4). Therefore, an array of tailor-made phosphines can be prepared easily through this direct methodology.

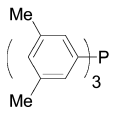
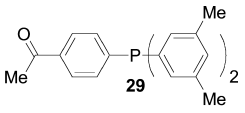
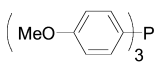
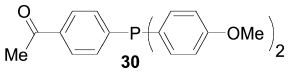
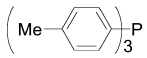
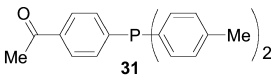
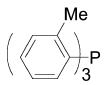
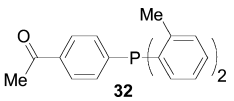
The yields of the phosphination remained low despite the operational simplicity. All aryl triflates were consumed completely. We did not observe the formation of any Ar_2PhP in the reaction of Ph_3P with ArOTf. Other side reactions such as reduction of ArOTf or unfavorable equilibrium (see mechanistic discussion) may account for the low yield.

A user-friendly and environmentally benign phosphination was successfully carried out in solvent-free conditions (Table 3).[22] No significant electronic effect was observed in the solvent-free phosphination since both electron-withdrawing and -donating substrates exhibited similar reaction rates (Table 3). Aryl nonaflate was found to be effective in this reaction (Table 3, entry 5). *ortho*-Substituted aryl

Table 2. Palladium-catalyzed phosphination of 4-acetophenyl triflate with triarylphosphines

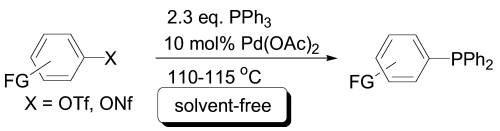


(3)

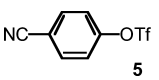
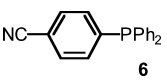
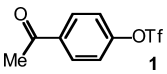
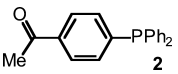
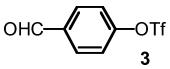
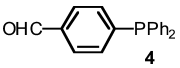
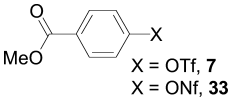
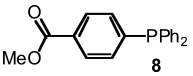
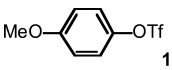
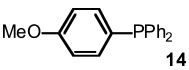
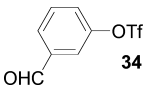
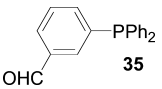
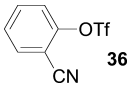
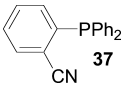
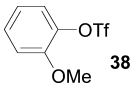
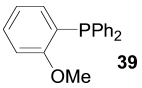
Entry	PAf_3	Products	Time (h)	Percentage yield[a]
1		 **29**	8	28
2		 **30**	6	24
3		 **31**	8	30
4		 **32**	72	No rxn[b]

[a] Isolated yields were reported.
[b] Starting material remained.

Table 3. Palladium-catalyzed phosphination under solvent-free conditions



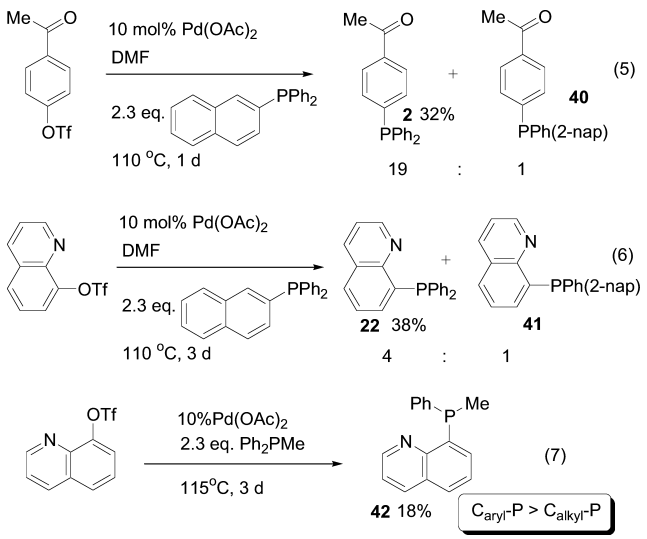
(4)

Entry	Substrate	Product	Time (d)	Percentage yield[a]
1	 **5**	 **6**	1.0	38
2	 **1**	 **2**	1.0	40
3	 **3**	 **4**	2.5	42
4	 X = OTf, **7** X = ONf, **33**	 **8**	1.5	42
5			1.5	43
6	 **13**	 **14**	0.8	26
7	 **34**	 **35**	1.5	38
8	 **36**	 **37**	2.5	37
9	 **38**	 **39**	3.5	27

[a] Isolated yields were reported.

triflates reacted in solvent-free conditions to give the desired phosphine products (Table 3, entries 8–9). In contrast, the corresponding *ortho*-substituted aryl bromides did not react in these reaction conditions. The rates of the reactions in solvent-free conditions were slower than that in DMF. Presumably, the high viscosity of the reaction mixture was responsible. As Ph_3P melted at 79°C, at the reaction temperature of 110°C, triphenylphosphine behaved as the solvent, ligands and phosphinating agents.

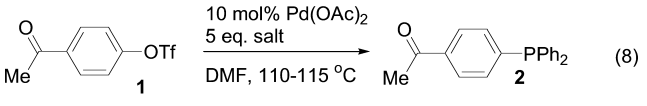
The selectivity of the phosphination can be observed when naphthyldiphenylphosphine was used as the phosphinating agent (Scheme 2). A 19:1 ratio of compounds **2**–**40** was obtained for 4-acetophenyl triflate substrate (Scheme 2, Eq. (5)). On the other hand, when a sterically more hindered 8-quinolyl triflate was used, the selectivity decreased to the ratio of 4:1 (**22**–**41**) (Scheme 2, Eq. (6)). Selective C_{aryl}–P>C_{alkyl}–P activation was observed when diphenylmethylphosphine was used as the phosphinating agent for quinolyl triflate (Scheme 2, Eq. (6)). The ease of C_{aryl}–P bond cleavage was possibly due to the preferred oxidative addition of less hindered C_{aryl}–P bond over the C_{alkyl}–P bond.[23] Moreover, the formation of a more stable Pd-aryl than Pd-alkyl intermediate was also a factor. Therefore, only 8-(methylphenyl)phosphino-quinoline (**42**) product was detected from GC-MS. The lower yield of the product was likely due to its air-sensitivity during purification.



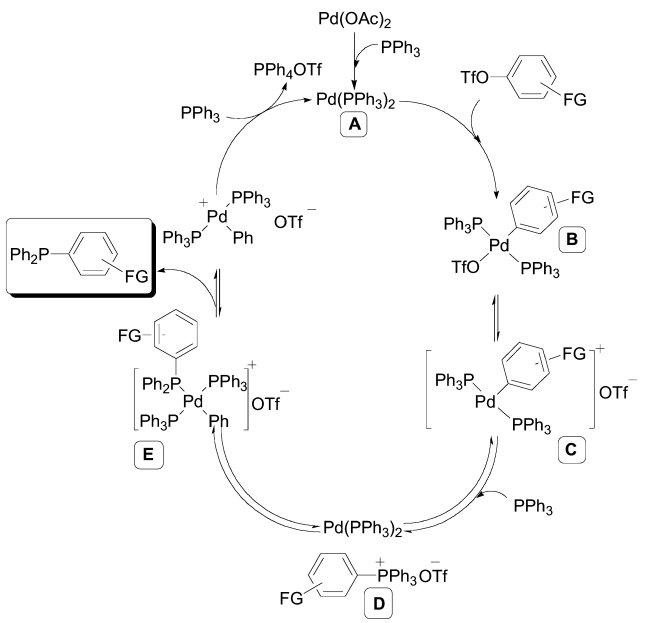
Scheme 2. Selectivities in palladium-catalyzed phosphination of aryl triflates.

The promoting effect of iodide[24] in transition metal-catalyzed reaction was not observed in this phosphination. Upon the addition of NaI, the rate and yield of phosphination were lowered (Eq. (8)). No 4-iodoacetophenone was detected by GC-MS analysis during the course of the reaction. The suppressing effect was likely caused by the reduction in the rate of added iodide in the Pd-aryl/P-aryl exchange through the formation of Pd-iodide complex,[25] which is very likely the rate determining step in the catalysis.

Scheme 3 illustrates a plausible mechanism for the reaction involving Pd(0)/Pd(II) cycles. Palladium(II) acetate is in

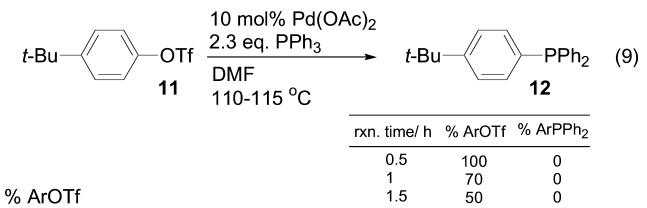


salt	time/h	%yield
--	2	38
NaI	48	12
NaI	96	16



Scheme 3. Suggested mechanism for palladium-catalyzed phosphination.

situ reduced by triphenylphosphine to form complex **A**, PdL_2 (L=triphenylphosphine).[26,27] This active palladium complex **A** then undergoes oxidative addition with functionalized aryl triflates to afford palladium complex **B** (Scheme 3).[28] The complex **C** subsequently undergoes reductive elimination with triphenylphosphine to produce a phosphonium salt **D** and palladium complex **A**. Such Pd-catalyzed phosphonium salt formation for *meta*- and *para*- but not *ortho*-substituted aryl bromides has been



rxn. time/ h	% ArOTf	% ArPPh2
0.5	100	0
1	70	0
1.5	50	0
2	38	3
3	23	18
4	19	23
5	9	31
6	0	48
7		43
8		42
9		40

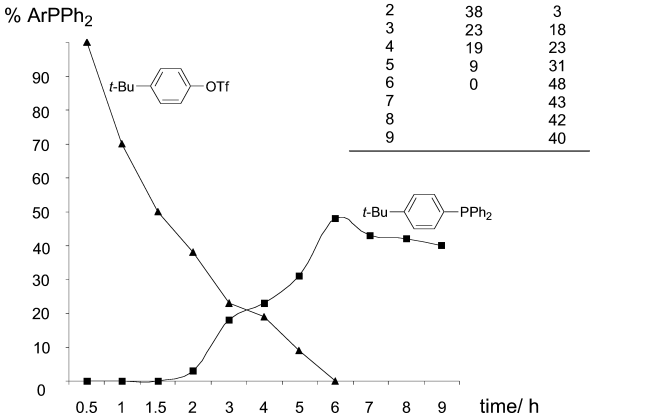


Figure 2. GC time profile for palladium-catalyzed phosphination.

reported.[29] The GC time profile for palladium-catalyzed phosphination showed that, the consumption of aryl triflate **11** occurred at the first 2 h of the reaction without any phosphine product **12** formed (Fig. 2). These data likely supported the rapid formation of phosphonium salt intermediate before the formation of product (Fig. 2).

The palladium complex **A** then undergoes oxidative addition by carbon–phosphorus bond cleavage of the phosphonium salt **D** to generate the coordinated $ArPPh_2$ Pd-complex (Scheme 3).[30,31] Finally, ligand substitution by triphenylphosphine to Pd(II) complex **E** gives $ArPPh_2$ and Pd–phenyl complex **G**. The PdL_2 species is regenerated by reductive elimination of triphenylphosphine and Pd bound phenyl group to yield the tetraphenylphosphonium triflate co-product (Scheme 3). Although the tetraphenylphosphonium salt was not isolated, it was detected by ^{31}P NMR (δ=24.0 ppm)[32] in the crude reaction mixture. Therefore, 2 equiv. of PPh_3 were required. The first one serves as the diphenylphosphinating agent and the second one yields the phosphonium salt co-product.

In conclusion, a catalytic user-friendly phosphination using triarylphosphines as the phosphinating reagents was developed and optimized. This carbon–phosphorus bond formation was compatible with a number of functional groups, including aldehyde, keto, ester, nitrile, ether, pyridine and etc. This phosphination employed air-stable triphenylphosphine as the phosphinating reagent, and the reaction was also carried out in neutral media. This process has a great potential to access a variety of substituted phosphines from the reaction of triarylphopshines with various functionalized aryl triflates.

3. Experimental

3.1. General considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. Dichloromethane and pyridine were distilled from anhydrous calcium chloride under nitrogen. *N,N*-Dimethylformamide was distilled from magnesium sulfate under reduced pressure.[33] Thin layer chromatography was performed on Merck precoated silica gel 60 F_{254} plates. Silica gel (Merck, 70–230 and 230–400 mesh) was used for column chromatography. ^1H NMR spectra were recorded on a Bruker DPX 300 (300 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 0.00 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were recorded on a Bruker DPX 300 (75 MHz) spectrometer and referenced to $CDCl_3$ (δ 77.00 ppm). ^{31}P NMR spectra were recorded on a Varian 400 (162 MHz) and referenced to 85% H_3PO_4 externally. Coupling constants (J) were reported in Hertz (Hz). Mass spectra (EIMS and FABMS) were recorded on a HP 5989B Mass Spectrometer. High resolution mass spectra (HRMS) were obtained on a Bruker APEX 47e FT-ICR mass spectrometer (ESIMS). GC-MS analyses were conducted on a HP G1800C GCD system using a HP5MS column (30 m×0.25 mm). The GC yields of the products were estimated using authentic samples together with anthracene as the internal standard.

3.2. General procedure for preparation of aryl triflates

4-Nitrophenol (0.5 g, 3.6 mmol) was dissolved in dry dichloromethane (20 mL) under nitrogen at room temperature followed by the addition of dry pyridine (0.87 mL, 10.8 mmol). Trifluoromethanesulfonic anhydride (triflic anhydride) (0.67 mL, 4.0 mmol) in dry dichloromethane (10 mL) was then added dropwise. The color of the solution was changed from yellow to orange with white fume evolved. The reaction mixture was allowed to stir at room temperature for an hour. Water (20 mL) was then added and the reaction mixture was extracted with dichloromethane (3×15 mL). The combined organic phase was washed with diluted hydrochloric acid, water, brine and dried over $MgSO_4$. The residue after rotary evaporation was purified by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate=3:1) as the eluent to obtain the 4-nitrophenyltrifluoromethanesulfonate (878 mg, 90%) as a pale yellow solid. R_f=0.7 (hexane/ethyl acetate=3:1); mp 52–54°C (lit.[46] 52–55°C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (dd, 2 H, J=1.4, 7.8 Hz), 8.37 (dd, 2H, J=1.4, 7.9 Hz); MS (EI): m/z (relative intensity) 271 (M^+, 100), 255 (17), 225 (40), 138 (67).

3.3. General procedure for palladium-catalyzed phosphination (methods A) and solvent-free palladium-catalyzed phosphination (methods B)

Method A. 4-Cyanophenyltrifluoromethanesulfonate (251 mg, 1.0 mmol), palladium(II) acetate (22.4 mg, 0.1 mmol), triphenylphosphine (603 mg, 2.3 mmol) were dissolved in DMF (2 mL) in a Teflon screw-capped flask under nitrogen. The reaction mixture was heated to 110–115°C for 2 h and the color of the solution was changed from pale yellow to red. 4-(Diphenylphosphino)benzonitrile was obtained (108 mg, 38%) as a white solid after purified by column chromatography on silica gel.

Method B. 4-Cyanophenyltrifluoromethanesulfonate (126 mg, 0.5 mmol), palladium(II) acetate (11.2 mg, 0.05 mmol) and triphenylphosphine (301 mg, 1.15 mmol) were mixed in a Teflon screw-capped flask under nitrogen. The reaction mixture was heated to 110–115°C to yield 4-(diphenylphosphino)benzonitrile (55 mg, 38%) as a white solid.

3.3.1. 4-Acetylphenyltrifluoromethanesulfonate (1).[34] The general procedure for synthesis of aryl triflate was used. 4-Hydroxyacetophenone (2.7 g, 20.0 mmol), pyridine (4.8 mL, 40.0 mmol), triflic anhydride (3.7 mL, 22.0 mmol) and dry CH_2Cl_2 were used to yield 4-acetylphenyltrifluoromethanesulfonate (**1**) (4.6 g, 87%) as a colorless liquid. R_f=0.41 (hexane/ethyl acetate=5:1); ^1H NMR (300 MHz, $CDCl_3$) δ 2.65 (s, 3H), 7.43 (d, 2H, J=8.7 Hz), 8.00 (d, 2H, J=8.4 Hz); MS (EI): m/z (relative intensity) 268 (M^+, 48), 189 (100), 161 (42).

3.3.2. 4-(Diphenylphosphino)acetophenone (2).[35] *Method A*. 4-Acetylphenyltriflate (**1**) (134 mg, 0.5 mmol),

palladium(II) acetate (11.2 mg, 0.05 mmol), triphenylphosphine (301 mg, 1.15 mmol) and DMF (2 mL) were used to yield 4-(diphenylphosphino)acetophenone (**2**) (56 mg, 37%) as a white solid. R_f=0.3 (hexane/ethyl acetate=15:1); mp 115–118°C (lit. 115–116°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.57 (s, 3H), 7.29–7.38 (m, 12H), 7.88 (dd, 2H, J=1.3, 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.6, 127.9 (d, J_{CP}=6.2 Hz), 128.6 (d, J_{CP}=7.2 Hz), 129.1, 133.2 (d, J_{CP}=18.5 Hz), 133.9 (d, J_{CP}=19.9 Hz), 135.9 (d, J_{CP}=10.4 Hz), 136.7, 144.3 (d, J_{CP}=14.2 Hz), 197.8; MS (EI): *m/z*(relative intensity) 304 (M^+, 100), 289 (10), 261 (12), 227 (11), 183 (90), 152 (30).

3.3.3. 4-Trifluoromethanesulfonyloxybenzaldehyde (3).[34] The general procedure for synthesis of aryl triflate was used. 4-Hydroxybenzaldehyde (732 mg, 6.0 mmol), pyridine (1.5 mL, 18.0 mmol), triflic anhydride (1.1 mL, 6.6 mmol) and dry CH_2Cl_2 (15 mL) were used to yield 4-trifluoromethane-sulfonyloxybenzaldehyde (**3**) (944 mg, 85%) as a colorless liquid. R_f=0.5 (hexane/ethyl acetate=4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, 2H, J=8.7 Hz), 7.99 (d, 2H, J=8.4 Hz), 10.03 (s, 1H); MS (EI): *m/z* (relative intensity) 254 (M^+, 80), 189 (100), 161 (12).

3.3.4. 4-(Diphenylphosphino)benzaldehyde (4).[36] *Method A*. 4-Trifluoromethane-sulfonyloxybenzaldehyde (**3**) (127 mg, 0.5 mmol), palladium(II) acetate (11.2 mg, 0.05 mmol), triphenylphosphine (301 mg, 1.15 mmol) and dry DMF (2 mL) were used to yield the 4-(diphenylphosphino)benzaldehyde (**4**) (45 mg, 31%) as a white solid. R_f=0.6 (hexane/ethyl acetate=10:1); mp=109–111°C (lit. 109–112°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.43 (m, 12H), 7.80 (dd, 2H, J=1.5, 8.1 Hz), 10.00 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.8 (d, J_{CP}=7.2 Hz), 129.3, 133.5 (d, J_{CP}=18.3 Hz), 134.0 (d, J_{CP}=20.0 Hz), 135.7 (d, J_{CP}=10.4 Hz), 136.0, 146.5 (d, J_{CP}=15.5 Hz), 191.9; ^{31}P (162 MHz, $CDCl_3$) δ −3.41; MS (EI): *m/z* (relative intensity) 290 (M^+, 100), 261 (8), 211 (9), 183 (95), 165 (12), 152 (20).

3.3.5. 4-Cyanophenyltrifluoromethanesulfonate (5).[34] The general procedure for synthesis of aryl triflate was used. 4-Cyanophenol (0.71 g, 6.0 mmol), pyridine (1.5 mL, 18.0 mmol), triflic anhydride (1.1 mL, 6.6 mmol) and dry dichloromethane (20 mL) were used to afford 4-cyanophenyl-trifluoromethanesulfonate (**5**) (1.4 g, 96%) as a colorless oil. R_f=0.6 (hexane/ethyl acetate=3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (dd, 2H, J=8.7, 12.0 Hz), 7.12 (dd, 2H, J=8.6, 12.0 Hz); MS (EI): *m/z* (relative intensity) 251 (M^+, 44), 211 (100), 173 (28).

3.3.6. 4-(Diphenylphosphino)benzonitrile (6).[37] *Method A*. 4-Cyanophenyltrifluoro-methanesulfonate (**5**) (251 mg, 1.0 mmol), palladium(II) acetate (22.4 mg, 0.1 mmol), triphenylphosphine (603 mg, 2.3 mmol) were dissolved in DMF (2 mL) in a Teflon screw-capped flask under nitrogen. The reaction mixture was heated to 110–115°C for 2 h and the color of the solution was changed from pale yellow to red. 4-(Diphenylphosphino)benzonitrile (**6**) was obtained (108 mg, 38%) as a white solid after purified by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate=10:1) as the eluent. R_f=0.6 (hexane/ethyl acetate=10:1); mp 120–122°C (lit. 120–122°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.39 (m, 12H), 7.57 (dd, 2 H, J=1.2, 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 111.8, 118.9, 128.8 (d, J_{CP}=7.4 Hz), 129.5, 131.7 (d, J_{CP}=5.9 Hz), 133.4 (d, J_{CP}=18.4 Hz), 134.0 (d, J_{CP}=20.2 Hz), 135.3 (d, J_{CP}=10.3 Hz), 145.1 (d, J_{CP}=16.5 Hz); MS (EI): *m/z* (relative intensity) 287 (M^+, 100), 208 (55), 195 (8), 183 (62), 177 (12).

3.3.7. Methyl 4-trifluoromethanesulfonyloxybenzoate (7).[34] The general procedure for synthesis of aryl triflate was used. Methyl 4-hydroxybenzoate (913 mg, 6 mmol), pyridine (1.5 mL, 18.0 mmol), triflic anhydride (1.1 mL, 6.6 mmol) and dry CH_2Cl_2 (20 mL) were used to yield methyl 4-trifluoromethanesulfonyloxybenzoate (**7**) (1.6 g, 91%) as a colorless liquid. R_f=0.52 (hexane/ethyl acetate=5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.92 (s, 3H), 7.34 (dt, 2H, J=2.4, 9.0 Hz), 8.13 (dt, 2H, J=2.3, 9.0 Hz); MS (EI): *m/z* (relative intensity) 284 (M^+, 46), 253 (77), 189 (100), 161 (17).

3.3.8. Methyl 4-(diphenylphosphino)benzoate (8).[38] Methyl 4-trifluoromethane-sulfonyloxybenzoate (**7**) (142 mg, 0.5 mmol), palladium(II) acetate (11.2 mg, 0.05 mmol), triphenylphosphine (301 mg, 1.15 mmol) and dry DMF (2 mL) were used to yield methyl 4-(diphenylphosphino)benzoate (**8**) (47 mg, 30%) as a white solid after purified by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate=10:1) as the eluent. R_f=0.6 (hexane/ethyl acetate=10:1); mp 105–107°C (lit. 105–107°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28–7.38 (m, 12H), 7.97 (dd, 2H, J=1.5, 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 128.7 (d, J_{CP}=7.1 Hz), 129.1, 129.3 (d, J_{CP}=6.4 Hz), 133.0, 133.1 (d, J_{CP}=18.5 Hz), 133.9 (d, J_{CP}=19.9 Hz), 136.1 (d, J_{CP}=10.5 Hz), 144.0 (d, J_{CP}=14.0 Hz), 166.9; MS (EI): *m/z* (relative intensity) 320 (M^+, 100), 289 (8), 261 (7), 207 (9), 183 (70), 166 (12).

3.3.9. 4-Chlorophenyltrifluoromethanesulfonate (9).[39] The general procedure for synthesis of aryl triflate was used. 4-Chlorophenol (0.64 g, 5.0 mmol), pyridine (1.2 mL, 15.0 mmol), triflic anhydride (0.87 mL, 5.2 mmol) and dry CH_2Cl_2 (20 mL) were used to yield 4-chlorophenyltrifluoromethanesulfonate (**9**) (1.21, 93%) as a colorless oil. R_f=0.3 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (dd, 2H, J=8.7, 12.0 Hz), 7.64 (dd, 2H, J=8.6, 12.0 Hz); MS (EI): *m/z* (relative intensity) 262 (M^+, 80), 260 (27), 225 (33), 127 (66).

3.3.10. 1-(Diphenylphosphino)-4-chlorobenzene (10).[40] 4-Chlorophenyltrifluoromethane-sulfonate (**9**) (130 mg, 0.5 mmol), palladium(II) acetate (11.2 mg, 0.05 mmol), triphenylphosphine (301 mg, 1.15 mmol), anthracene (internal standard) (89 mg, 0.5 mmol), and DMF (2 mL) were used to yield the 1-(diphenylphosphino)-4-chlorobenzene (**10**) (45% GC yield), and the yield was determined by GC with respected to the calibration curve of the authentic sample and anthracene.

3.3.11. 4-*tert*-Butylphenyltrifluoromethanesulfonate (11).[41] The general procedure for synthesis of aryl triflate was used. 4-*tert*-Butylphenol (0.75 g, 5.0 mmol), pyridine (1.2 mL, 15.0 mmol), triflic anhydride (0.87 mL, 5.2 mmol) and dry CH_2Cl_2 (20 mL) were used to yield

4-*tert*-butylphenyltrifluoromethanesulfonate (**11**) (1.3 g, 90%) as a colorless oil. R_f=0.5 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (s, 9H), 7.18 (dd, 2H, J=8.7, 12.1 Hz), 7.44 (dd, 2H, J=8.6, 12.0 Hz); MS (EI): m/z (relative intensity) 282 (M^+, 100), 225 (67), 149 (55).

3.3.12. 1-(Diphenylphosphino)-4-*tert*-butylbenzene (12).[42] 4-*tert*-Butylphenyltrifluoro-methanesulfonate (**11**) (141 mg, 0.5 mmol), palladium(II) acetate (11.2 mg, 0.05 mmol), triphenylphosphine (301 mg, 1.15 mmol) and internal standard anthracene (89 mg, 0.5 mmol) were dissolved in DMF (2 mL) in a Telfon screw-capped flask under nitrogen. The reaction mixture was heated to 110–115°C for 6 h and the color of the solution was changed from pale yellow to orange. The reaction was cooled down and the yield of 1-(diphenylphosphino)-4-*tert*-butylbenzene (**12**) (50% GC yield) was determined by GC with respected to the calibration curve of the authentic sample and anthracene.

3.3.13. 4-Methoxyphenyltrifluoromethanesulfonate (13).[39] The general procedure for synthesis of aryl triflate was used. 4-Methoxyphenol (248 mg, 2.0 mmol), pyridine (0.48 mL, 6.0 mmol), triflic anhydride (0.37 mL, 2.2 mmol) and dry CH_2Cl_2 (15 mL) were used to yield 4-methoxyphenyltrifluoromethanesulfonate (**13**) (450 mg, 88%) as a pale yellow liquid. R_f=0.56 (hexane/ethyl acetate=5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.91 (d, 2H, J=9.0 Hz), 7.18 (d, 2H, J=9.3 Hz), 7.28–7.31 (m, 1H); MS (EI): m/z (relative intensity) 254 (M^+, 33), 215 (11), 161 (17), 133 (49), 69 (100).

3.3.14. 4-(Diphenylphosphino)anisole (14).[43] *Method A*. 4-methoxyphenyl-trifluoromethanesulfonate (**13**) (128 mg, 0.5 mmol), palladium(II) acetate (11.2 mg, 0.05 mmol), triphenylphosphine (301 mg, 1.15 mmol) and dry DMF (2 mL) were used to yield 4-(diphenylphosphino)anisole (**14**) (29 mg, 20%) as a white solid; mp 101–104°C (lit.[43] 101–103°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 3H), 7.10 (dd, 2H, J=4.0, 8.1 Hz), 7.24–7.59 (m, 12H); MS (EI): m/z (relative intensity) 292 (M^+, 100), 277 (12), 259 (10), 215 (30), 183 (48).

3.3.15. 2-Methoxyphenyltrifluoromethanesulfonate (15).[39] The general procedure for synthesis of aryl triflate was used. 2-Methoxyphenol (1.1 g, 10.0 mmol), pyridine (2.4 mL, 20.0 mmol), triflic anhydride (1.9 mL, 11.0 mmol) and dry CH_2Cl_2 (20 mL) were used to yield 2-methoxyphenyltrifluoromethanesulfonate (**15**) (2.1 g, 82%) as a colorless liquid. R_f=0.54 (hexane/ethyl acetate=10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.80 (t, 1H, J=2.4 Hz), 6.85–6.95 (m, 2H), 7.35 (t, 1H, J=8.3 Hz); MS (EI): m/z (relative intensity) 256 (M^+, 27), 209 (58), 108 (100).

3.3.16. 2-(Diphenylphosphino)anisole (16).[43] *Method A*. 2-Methoxyphenyltrifluoromethanesulfonate (**15**) (128 mg, 0.5 mmol), palladium(II) acetate (11 mg, 0.05 mmol), triphenylphosphine (301 mg, 1.15 mmol) and dry DMF (2 mL) were used to yield 2-(diphenylphosphino)anisole (**16**) (40 mg, 28%) as a white solid; mp 95–98°C (lit. 95–98°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.48 (s, 3H), 7.05 (dd, 2H, J=4.0, 8.1 Hz), 7.24–7.59 (m, 12H); MS (EI): m/z (relative intensity) 292 (M^+, 100), 277 (18), 259 (12), 215 (30), 183 (48).

3.3.17. 2-Naphthyltrifluoromethanesulfonate (17).[39] The general procedure for synthesis of aryl triflate was used. 2-Naphthol (577 mg, 4.0 mmol), pyridine (1 mL, 12.0 mmol), triflic anhydride (0.7 mL, 4.2 mmol) and dry dichloromethane (30 mL) were used to yield the 2-naphthyltrifluoromethansulfonate (**17**) (928 mg, 92%) as a colorless liquid. R_f=0.6 (hexane/ethyl acetate=4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, 1H, J=1.3, 7.8 Hz), 7.59 (d, 1H, J=7.9 Hz), 7.32–7.55 (m, 5H); MS (EI): m/z (relative intensity) 276 (M^+, 100), 143 (86).

3.3.18. 2-(Diphenylphosphino)naphthalene (18).[40] 2-Naphthyltrifluoromethanesulfonate (**17**) (138 mg, 0.5 mmol), palladium(II) acetate (11.2 mg, 0.05 mmol), triphenylphosphine (301 mg, 1.15 mmol), anthracene (internal standard) (89 mg, 0.5 mmol), and DMF (2 mL) were used to yield the 2-(diphenylphosphino)naphthalene (**18**) (51% GC yield) was determined by GC with respected to the calibration curve of the authentic sample and anthracene.

3.3.19. 3-Pyridyltrifluoromethanesulfonate (19).[44] 3-Hydroxypyridine (0.5 g, 5.3 mmol) was dissolved in anhydrous dichloromethane (10 mL) under nitrogen at room temperature followed by the addition of dry pyridine (1.3 mL, 15.9 mmol). Triflic anhydride (0.98 mL, 5.8 mmol) in dichloromethane (3 mL) was then added dropwise. The color of the solution was changed from orange to red with white fume evolved. The reaction mixture was allowed to stir at room temperature for one hour. Water (20 mL) was added, extracted with dichloromethane (3×30 mL). The combined organic phase was washed with water, brine and dried over $MgSO_4$. The residue was purified by short column chromatography on silica gel to afford the 3-pyridyltrifluoromethanesulfonate (**19**) (1.08 g, 90%) as a pale yellow oil. R_f=0.3 (hexane/ethyl acetate=3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, 1H, J=1.5 Hz), 8.43 (d, 1H, J=8.0 Hz), 7.66 (t, 1H, J=8.0 Hz), 7.35 (d, 1H, J=7.9 Hz); MS (EI): m/z (relative intensity) 227 (M^+, 100), 158 (10), 94 (70).

3.3.20. 3-(Diphenylphosphino)pyridine (20).[34] 3-Pyridyl trifluoromethanesulfonate (**19**) (1.14 g, 5.0 mmol), palladium(II) acetate (112 mg, 0.5 mmol), triphenylphosphine (3.01 g, 11.5 mmol) were dissolved in dry DMF (20 mL) in a Telfon screw-capped flask under nitrogen. The reaction was heated to 110–115°C for 24 h and the color of the solution was changed from pale yellow to deep red. The reaction mixture was cooled down and filtered over a short silica gel pad and the pad was washed by dichloromethane. The aqueous extraction was performed by using hydrochloric acid (3 M, 150 mL×5) and the aqueous phase was collected and neutralized by sodium carbonate solution to pH 7–8. The aqueous solution was extracted by dichloromethane (50 mL×3). The combined organic phase was washed with brine and dried over $MgSO_4$. The 3-(diphenylphosphino)pyridine (**20**) (263 mg, 20%) was obtained as the pale yellow solid. R_f=0.8 (hexane/ethyl acetate=5:1); mp=98–100°C (lit. 98–100°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, 1H, J=1.4 Hz), 8.30 (d, 1H, J=8.3 Hz), 7.92 (t, 1H, J=8.2 Hz), 7.27–7.69 (m, 11H); MS (EI): m/z (relative intensity) 263 (M^+, 100), 186 (20).

3.3.21. 8-Quinonyltrifluoromethanesulfonate (21).[45] The general procedure of trifluoromethanesulfonation was used. 8-Hydroxylquinoline (0.5 g, 3.5 mmol), pyridine (0.83 mL, 10.4 mmol), triflic anhydride (0.64 mL, 3.8 mmol) and dry dichloromethane (20 mL) were used to afford the 8-quinonyltrifluoromethanesulfonate (**21**) (878 mg, 92%) as a pale yellow solid. R_f=0.4 (hexane/ethyl acetate=3:1); mp 70–73°C (lit.[45] 70–72°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.50 (d, 1H, J=1.5 Hz), 7.87 (d, 1H, J=8.1 Hz), 7.34–7.67 (m, 4H); MS (EI): m/z (relative intensity) 277 (M^+, 100), 144 (54).

3.3.22. 8-(Diphenylphosphino)quinoline (22).[34] 8-Quinolyltrifluoromethanesulfonate (**21**) (554 mg, 2.0 mmol), palladium(II) acetate (45 mg, 0.2 mmol), triphenylphosphine (1.21 g, 4.6 mmol) were dissolved in dry DMF (8 mL) in a Telfon screw-capped flask under nitrogen. The reaction was heated to 110–115°C for 72 h and the color of the solution was changed from yellow to red. The reaction mixture was cooled down and concentrated by reduced pressure. The residue was purified by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate=5:1) as eluent to afford 8-(diphenylphosphino)quinoline (**22**) (282 mg, 45%) as the pale yellow solid. R_f=0.5 (hexane/ethyl acetate=5:1); mp 134–136°C (lit. 133–136°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10–7.14 (m, 1H), 7.26–7.43 (m, 12H), 7.78 (d, 1H, J=8.0 Hz), 8.12 (d, 1H, J=8.2 Hz), 8.85 (dd, 1H, J=1.6, 4.2 Hz), ^{31}P NMR (162 MHz, $CDCl_3$) δ −15.11; MS (EI): m/z (relative intensity) 313 (M^+, 100), 235 (60), 204 (51), 183 (32), 159 (30).

3.3.23. 4-Nitrophenyltrifluoromethanesulfonate (23).[46] As shown in general procedure.

3.3.24. 1,4-Ditrifluoromethanesulfonyloxybenzene (25).[39] The general procedure for synthesis of aryl triflate was used. 1,4-Dihydroxybenzene (550 mg, 5.0 mmol), pyridine (2.4 mL, 30.0 mmol), triflic anhydride (2 mL, 12.0 mmol) and dry CH_2Cl_2 (20 mL) were used to yield 1,4-ditrifluoromethanesulfonyloxybenzene (**25**) (1.8 g, 95 %) as a white solid. After purified by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate=5:1) as the eluent. R_f=0.74 (hexane/ethyl acetate=5:1); mp 53–55°C (lit. 52–55°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.4 (s, 4H); MS (EI): m/z (relative intensity) 374 (M^+, 43), 189 (100), 133 (49).

3.3.25. 4-(Bis(3,5-dimethylphenyl)phosphino)acetophenone (29). Method A was followed. 4-Acetylphenyltriflate (**1**) (1.0 mmol), palladium(II) acetate (22.4 mg, 0.1 mmol), trixylylphosphine (796 mg, 2.3 mmol) and dry DMF (4 mL) were used to yield 4-(bis(3,5-dimethyl)-phosphino)acetophenone (**29**) (122 mg, 34%) as pale yellow solid after purified by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate=10:1) as the eluent. R_f=0.6 (hexane/ethyl acetate=10:1); mp 56–58°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.27 (s, 12H), 2.59 (s, 3H), 6.93 (s, 2H), 6.96 (s, 2H), 7.00 (s, 2H), 7.34 (dd, 2H, J=8.3 Hz, 1.4 Hz), 7.87 (dd, 2H, J=8.3, 1.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 26.6, 127.9 (d, J_{CP}=6.2 Hz), 131.0, 131.7 (d, J_{CP}=20.2 Hz), 133.2 (d, J_{CP}=18.2 Hz), 135.7 (d, J_{CP}=9.5 Hz), 136.5, 138.1 (d, J_{CP}=7.9 Hz), 145.1 (d, J_{CP}=14.8 Hz), 198.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ −12.88; MS (EI): m/z (relative intensity) 360 (M^+, 100), 345 (8), 317 (12), 253 (8), 241 (15), 225 (13), 211 (22), 193 (16); HRMS (ESIMS) calcd for $C_{24}H_{25}OPH^+$ 361.1721, found 361.1709.

3.3.26. 4-(Di(4-methoxyphenyl)phosphino)acetophenone (30). Method A was followed. 4-Acetylphenyltriflate (**1**) (1.0 mmol), palladium acetate (22.4 mg, 0.1 mmol), tri(4-methoxyphenyl)phosphine (810 mg, 2.3 mmol) and dry DMF (4 mL) were used to yield 4-(di(4-methoxyphenyl)-phosphino)acetophenone (**30**) (120 mg, 33%) as pale yellow solid after purified by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate=10:1) as the eluent. R_f=0.2 (hexane/ethyl acetate=10:1); mp 54–56°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.57 (s, 3H), 3.81 (s, 6H), 6.90 (dd, 4H, J=6.0, 2.1 Hz), 7.25–7.32 (m, 6H), 7.85 (dd, 2H, J=8.4, 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.6, 55.2, 114.3 (d, J_{CP}=8.3 Hz), 127.1 (d, J_{CP}=7.4 Hz), 127.8 (d, J_{CP}=5.8 Hz), 132.6 (d, J_{CP}=17.7 Hz), 135.5 (d, J_{CP}=21.5 Hz), 136.3, 146.1 (d, J_{CP}=13.9 Hz), 160.5, 197.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ −13.03; MS (EI): m/z (relative intensity) 364 (M^+, 100), 349 (10), 281 (9), 257 (10), 245 (30), 229 (8), 214 (40), 199 (18); HRMS (ESIMS) calcd for $C_{22}H_{21}O_3PH^+$ 365.1307, found 365.1289.

3.3.27. 4-(Di(4-tolyl)phosphino)acetophenone (31). Method A was followed. 4-Acetylphenyltriflate (**1**) (1.0 mmol), palladium acetate (22.4 mg, 0.1 mmol), tri(4-tolyl)phosphine (699 mg, 2.3 mmol) and dry DMF (4 mL) were used to obtain 4-(di(4-tolyl)phosphino)acetophenone (**31**) (129 mg, 39%) as light yellow solid after purified by column chromatography on silica gel using a solvent mixture (hexane/ethyl acetate=10:1) as the eluent. R_f=0.4 (hexane/ethyl acetate=10:1); mp 58–60°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 6H), 2.57 (s, 3H), 7.15–7.25 (m, 8H), 7.36 (dd, 2H, J=8.4, 1.5 Hz), 7.86 (dd, 2H, J=8.4, 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 26.6, 127.9 (d, J_{CP}=6.0 Hz), 129.5 (d, J_{CP}=7.5 Hz), 132.7 (d, J_{CP}=9.0 Hz), 133.0 (d, J_{CP}=18.2 Hz), 134.0 (d, J_{CP}=20.3 Hz), 136.5, 139.2, 145.3 (d, J_{CP}=14.3 Hz), 197.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ −12.60; MS (EI): m/z (relative intensity) 332 (M^+, 100), 317 (5), 289 (10), 281 (7), 241 (8), 211 (30), 197 (28); HRMS (ESIMS) calcd for $C_{22}H_{21}OPH^+$ 333.1408, found 333.1385.

3.3.28. 3-(Diphenylphosphino)benzaldehyde (35).[47] Method B was followed. Yield 38%. R_f=0.6 (hexane/ethyl acetate=10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.43 (m, 12H), 7.80 (dd, 2H, J=8.1, 1.5 Hz), 10.00 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 128.8 (d, J_{CP}=7.2 Hz), 129.3, 133.5 (d, J_{CP}=18.3 Hz), 134.0 (d, J_{CP}=20.0 Hz), 135.7 (d, J_{CP}=10.4 Hz), 136.0, 146.5 (d, J_{CP}=15.5 Hz), 191.9; ^{31}P (162 MHz, $CDCl_3$) δ −3.41; MS (EI): m/z (relative intensity) 290 (M^+, 100), 261 (8), 211 (9), 183 (95), 165 (12), 152 (20).

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