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Synthesis of 3-Arylbenzofuran-2-yl Phosphines via Rhodium-Catalyzed Redox-Neutral C−H Activation and Their Applications in Palladium-Catalyzed Cross-Coupling of Aryl Chlorides

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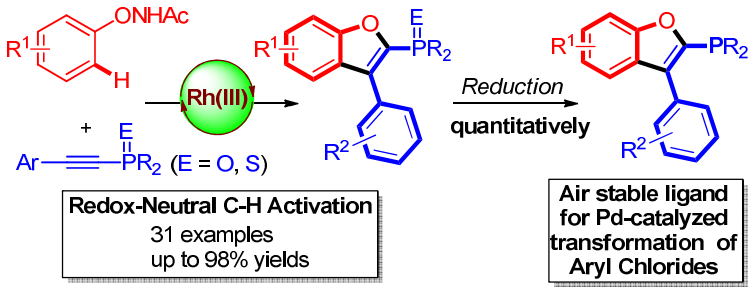


ABSTRACT: A new class of aryl-heteroarylphosphines, 3-arylbenzofuran-2-yl phosphines, were synthesized by [Cp*Rh(III)]-catalyzed redox-neutral cyclization of *N*-phenoxyacetamides with 1-alkynylphosphine sulfides and oxides followed by reduction. This step-economic reaction proceeds in excellent regioselectivity with a broad substrate scope. The application of the resulted air stable trivalent phosphine containing dicyclohexylphosphino moiety in palladium-catalyzed Suzuki-Miyaura coupling and Buchwald-Hartwig amination of aryl chlorides is also described.

INTRODUCTION

Since recognition of the significant effects of supporting ligands on the improvement of reactivity and stability of the catalyst, miscellaneous kinds of phosphines have been developed. Representatively, phosphine ligands based on the monophosphinobiaryl backbone[1] [Figure 1(a)], which were first introduced by the group of Buchwald for Pd-catalyzed cross-coupling in 1998,[1d] have been utilized in a wide variety of transition-metal-catalyzed carbon-carbon and carbon-heteroatom bonds formation reactions. The novel structure permits the fine-tuning of steric and electronic elements of the ligand. Density functional theory studies have also revealed that the interactions between palladium and the non-phosphine-containing ring of the ligand[2] [Figure 1(b)] can stabilize oxidative addition intermediates and facilitate the reduction elimination step.[3] Therefore, one class of heteroarylphosphine ligands with aryl-heteroaryl monophosphine as the main skeleton [Figure 1(c)] have been explored and identified as a unique type of supporting ligand for diverse transition-metal-catalyzed transformations.[4] In this context, a range of heteroaromatic compounds including imidazole,[5] pyrrole,[6] triazole,[7] indole,[8] and isoquinolinone[9] based phosphines [Figure 1(d)] have been designed and synthesized by the groups of Beller, Zhang, Kwong, Yorimitsu and Oshima, and others as well as ourselves. However, 3-arylbenzofuran-2-yl phosphines[10] [Figure 1(e)], to the best of our knowledge, have remained elusive until now.

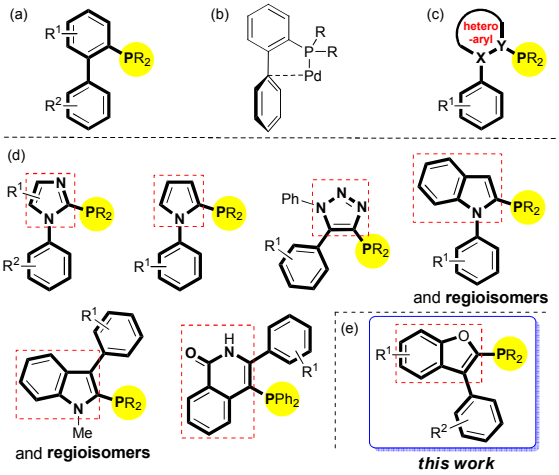
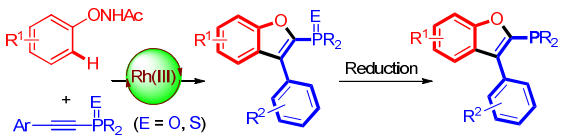


Figure 1. (a) Structural backbone for biarylphosphines; (b) Palladium-arene interaction; (c) Structural backbone for aryl-heteroarylphosphines; (d) Examples of previously developed aryl-heteroarylphosphines.

On the other hand, the conventional synthetic methods for heteroarylphosphines are mostly limited to the reactions of chlorophosphines with metalated heteroaromatic compounds. Consequently, it is demanding to prepare the proper heteroaromatic compounds prior to introduction of a phosphorus moiety, which commonly results in a multistep synthesis especially in cases the heteroaryl compounds are not commercially available. In recent years, Rh(III)-catalyzed oxidative coupling of C−H bonds with alkynes has been proven to be a straightforward and efficient approach to construct (hetero)cyclic compounds.[11] In this regard, we previously disclosed the oxidative coupling of *N*-(pivaloyloxy)benzamides with 1-alkynylphosphine sulfides under rhodium catalysis followed by desulfidation to afford phosphines containing an isoquinolin-1(*2H*)-one motif.[9] But this catalytic system suffered from two main issues: low regioselectivity for electron-rich benzamide substrates and poor reactivity for sterically bulky (1-alkynyl)dicyclohexylphosphine sulfide. In line with our interest in creation of new organophosphine species and transition-metal-catalyzed heterocycle synthesis through C−H coupling with alkynes,[9,12] described herein are our recent development of rhodium-catalyzed redox-neutral annulation of *N*-phenoxyacetamides[13] with 1-alkynylphosphine sulfides and oxides[8c,14] (Scheme 1). The present catalytic process introduces a phosphorus moiety and a substituent at the proper positions with concomitant formation of a benzofuranyl ring, which provides a step-economic and regioselective access to form 3-arylbenzofuran-2-yl phosphine derivatives. Note that, after reduction, the corresponding trivalent phosphine with dicyclohexylphosphino moiety could serve as an efficient supporting ligand for palladium-catalyzed Suzuki-Miyaura coupling and Buchwald-Hartwig amination of aryl chlorides.

Scheme 1. Rhodium-Catalyzed Oxidative Coupling of *N*-Phenoxyacetamides with 1-Alkynylphosphine Derivatives Followed by Reduction to Form 3-Arylbenzofuran Based 2-Phosphines



√ Redox-neutral C-H activation/annulation strategy

√ Step-economic and regioselective synthetic method

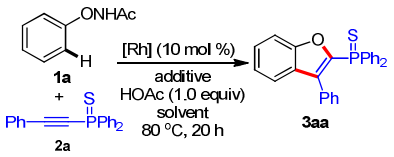
√ Broad substrate scope and good functional groups tolerance

√ New ligands for Pd-catalyzed cross-coupling reactions of ArCl

RESULTS AND DISCUSSION

We initiated our optimization experiments with the cyclization reaction of *N*-phenoxyacetamide (**1a**) with diphenyl(phenylethynyl)phosphine sulfide (**2a**) (Table 1). To our delight, treatment of **1a** with **2a** (1.5 equiv) in the presence of $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (10 mol %), CsOPiv (2 equiv), and HOAc (1 equiv) in DCM at 80 ^oC for 20 hours led to the formation of annulated product diphenyl(3-phenylbenzofuran-2-yl)phosphine sulfide (**3aa**) in moderate NMR yield (43%, entry 1). Importantly, the reaction occurred with virtually complete regioselectivity, as demonstrated by the detection of one single regioisomer from the crude reaction mixture by ^{31}P NMR. The structure of **3aa** was confirmed by NMR analysis and HRMS spectrometry, as well as X-ray crystallography (see Table 1 and the Supporting Information).[15] We then evaluated the effect of various reaction parameters for the benchmark reaction. As to the solvent, $CHCl_3$, MeOH, CH_3CN, and PhCl were less effective than DCM, while *t*AmOH, PhMe, DMSO, and DMF essential gave no products (entries 2-4 and Table S3 in the Supporting Information). Reserve the ratio of **1a**/**2a** to 1.2/1 slightly improved the efficieny (entry 6). Encouragingly, we found an enhanced chemical yield was achieved by addition of AgOAc (entry 9), which significantly increased the reactivity than other additive salts such as CsOPiv, CsOAc, and KOAc (entries 6-8). In addition, reducing the amount of AgOAc (to 0.5 equiv) slightly affected the outcome of the transformation (entry 10). It was observed that the ratio of 1.5/1 for **1a**/**2a** was most optimal, affording product **3aa** in 98% NMR yield and 93% isolated yield (entry 11). A decrease in the amount of catalyst resulted in lower conversion (entry 12). Furthermore, the reaction efficiency was not sensitive to the reaction temperatures (entry 13). $[Cp^*RhCl_2]_2$ is inferior to its cationic complex as catalyst (entry 14) and $[(p\text{-cymene})RuCl_2]_2$ was totally inactive under the present reaction conditions (entry 15).

Table 1. Optimization of Reaction Conditions[a]



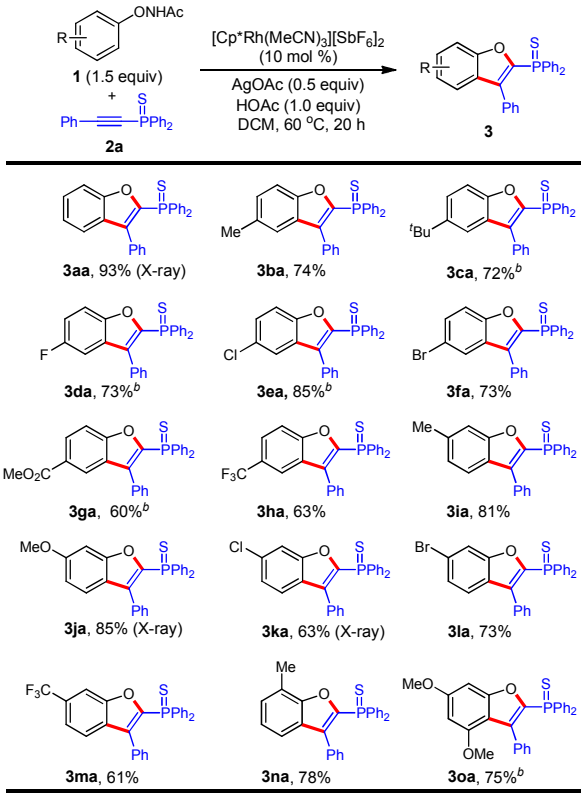
entry	1a/2a	additives (equiv)	solvent	yield (%)[b]
1	1/1.5	CsOPiv (2.0)	DCM	43
2	1/1.5	CsOPiv (2.0)	MeOH	26
3	1/1.5	CsOPiv (2.0)	$CHCl_3$	29
4	1/1.5	CsOPiv (2.0)	DMF	0
5	1/1.5	CsOPiv (2.0)	CH_3CN	13
6	1.2/1	CsOPiv (2.0)	DCM	53
7	1.2/1	CsOAc (2.0)	DCM	46
8	1.2/1	KOAc (2.0)	DCM	40
9	1.2/1	AgOAc (2.0)	DCM	96
10	1.2/1	AgOAc (0.5)	DCM	89
11	1.5/1	AgOAc (0.5)	DCM	98 (93)[c]
12[d]	1.5/1	AgOAc (0.5)	DCM	88
13[e]	1.5/1	AgOAc (0.5)	DCM	98 (93)[c]
14[f]	1.5/1	AgOAc (0.5)	DCM	90
15[g]	1.5/1	AgOAc (0.5)	DCM	0

[a]Reactions in 0.2 mmol scale (0.1 M), [Rh] = $[Cp^*Rh(MeCN)_3][SbF_6]_2$. [b]Yield of crude reaction mixture determined by ^{31}P NMR (internal standard: trimethyl phosphate). [c]Value in parentheses indicates isolated yield. [d][Rh] (5 mol %) was used as catalyst. [e]60 °C. [f]$[Cp^*RhCl_2]_2$ (5 mol %) was used as catalyst. [g]$[(p\text{-cymene})RuCl_2]_2$ (5 mol %) was used as catalyst. DCM = dichloromethane, DMF = *N*,*N*-dimethylformamide.

With the promising optimal conditions, the reaction scope of *N*-phenoxyacetamides was first investigated (Scheme 2). The annulation took place smoothly with *N*-phenoxyacetamides bearing diverse arene substituents to give the corresponding 2-diphenylthiophosphinyl-3-phenylbenzofuran derivatives in good to excellent yields. In this respect, both electron-rich and electron-poor *N*-phenoxyacetamides were nearly equally effective in this reaction and many important functional groups, including halides (**3da**−**fa**, **3ka**, and **3la**), ester (**3ga**), trifluoromethyl (**3ha** and **3ma**), and methoxy (**3ja** and **3oa**), remained intact under the reaction conditions. For substrates bearing *meta*-substituents, the catalytic process only occurred at the less steric hindered aromatic C-H bond (**3ia**−**ma**), as confirmed by X-ray crystallographic analysis of the structures of **3ja** and **3ka** (see the Supporting Information).[15] Additionally, *ortho*-substituted substrate **1n** and disubstituted substrate **1o** were also reacted to provide the desired products **3na** and **3oa**, respectively. It is worthwhile noting that all the generated products **3aa-oa** were formed as a single regioisomer with

diphenylthiophosphino moiety being installed at 2-position of benzofuran, thereby highlighting the excellent regioselectivity of the present catalytic system.

Scheme 2. Scope of *N*-phenoxyacetamides[a]

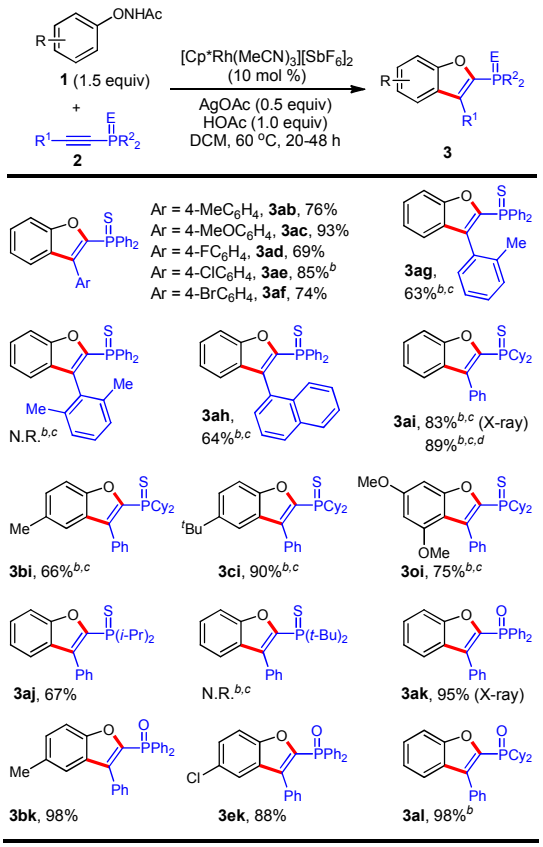


[a]Reactions in 0.2 mmol scale (0.1 M), yields of isolated products. [b]80 °C.

To further demonstrate the generality of this transformation, we next surveyed the scope with respect to 1-alkynylphosphine derivatives. The results are summarized in Scheme 3. Irrespective of the electronic nature of arene substituents, 1-alkynylphosphine sulfides **2b**–**f** were readily converted into products **3ab**–**af** (69-93%) in reactions with **1a**. While (*o*-tolylethynyl)diphenylphosphine sulfide **2g** is a suitable substrate to form **3ag** in good yield, the cyclization did not occur when ((2,6-dimethylphenyl)ethynyl)diphenylphosphine sulfide was employed. Gratifyingly, (1-naphthalenylethynyl)diphenylphosphine sulfide **2h** was also applicable for this reaction and the corresponding product **3ah** was isolated in reasonable yield. Notably, high conversion was achieved with (1-alkynyl)dicyclohexylphosphine sulfide **2i** although an increase of the stoichiometry of **1a** was required. Thus, bulky phosphine products **3ai**–**3ci** and **3oi** were obtained in 66-90% isolated yield. Furthermore, we prepared **3ai** in large scale with comparable yield (2.0 mmol, 89% yield), showing the preparative utility of this transformation. Alkyne **2j** with diisopropylthiophosphino

moiety was also a facile reactant for this catalytic process, whereas steric more bulky ditertbutylthiophosphino analogue led to no reaction at all. Not only were phosphine sulfides applicable to the reaction, but phosphine oxides worked as well. For example, 1-alkynylphosphine oxides PhCCP(O)R_2 (R = Ph, **1k**; R = cyclohexyl, **1l**) were verified to be active partners for the present annulation protocol, giving rise to the desired products **3ak**, **3bk**, **3ek**, and **3al** in high yields (88-98%). Again, excellent regioselectivety was observed for all phosphinoacetylenes employed with the formation of one single regioisomer. Moreover, the structures of **3ai** and **3ak** were unambiguously confirmed by X-ray crystallographic analysis (see the Supporting Information).[15]

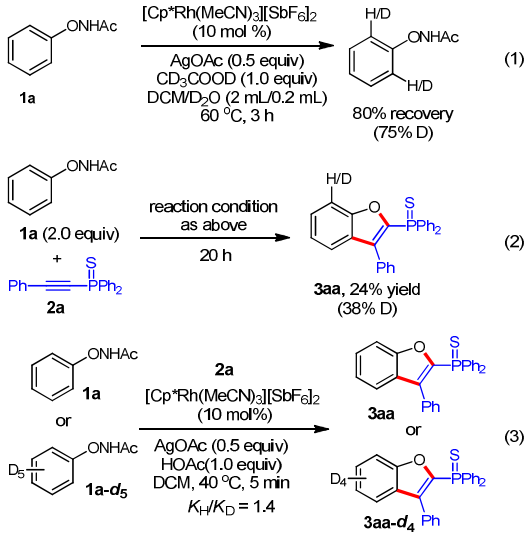
Scheme 3. Scope of (1-Alkynyl)diphenylphosphine Derivatives[a]



[a]Reactions in 0.2 mmol scale (0.1 M), yields of isolated products. [b]80 °C. [c]3.0 equiv of **1** was used. [d]Reaction in 2.0 mmol scale (0.2 M). N.R. = No Reaction.

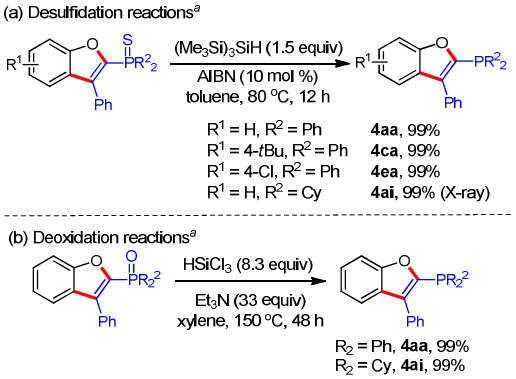
Subsequently, a series of experiments were carried out to gain insight into the mechanism of the current reaction (see the Supporting Information for details). First, **1a** was conducted with D_2O in the absence of alkyne and 75% deuterium was incorporated at the two *ortho*-positions of the

directing group (eq 1). When the same reaction was performed in the presence of **2a**, 38% deuterium incorporation was detected in product **3aa** (eq 2). These results suggested that, under the reaction conditions, a reversible cyclometalation mode was involved. A kinetic isotope effect (KIE) of k_H/k_D = 1.4 was observed in the intermolecular isotopic study of two parallel competition reactions between **1a** and [D_5]-**1a** (eq 3), thus demonstrating that the cleavage of the C−H bond is likely not involved in the rate-determining step.[16,17]



To our satisfaction, the annulated products, 2-benzofuranylphosphine sulfides and oxides, could be reduced smoothly. Under the radical desulfidation reaction conditions,[9,13b,18] the phosphine sulfides **3aa**, **3ca**, **3ea**, and **3ai** were converted into the corresponding trivalent phosphines quantitatively [Scheme 4(a)]. Meanwhile, treatment of the phosphine oxides **3ak** and **3al** with trichlorosilane and triethylamine also afforded the trivalent phosphines **4aa** and **4ai** in quantitative yield[19] [Scheme 4(b)]. It is important to note that the phosphines **4** are stable under air, thus allowing the purification by quick silica gel column chromatography without any special care. Particularly, even the solution of **4ai** are stable enough so that we could obtain the suitable single crystals for X-ray crystal structure analysis by recrystallization of **4ai** in EtOAc open to air.[15]

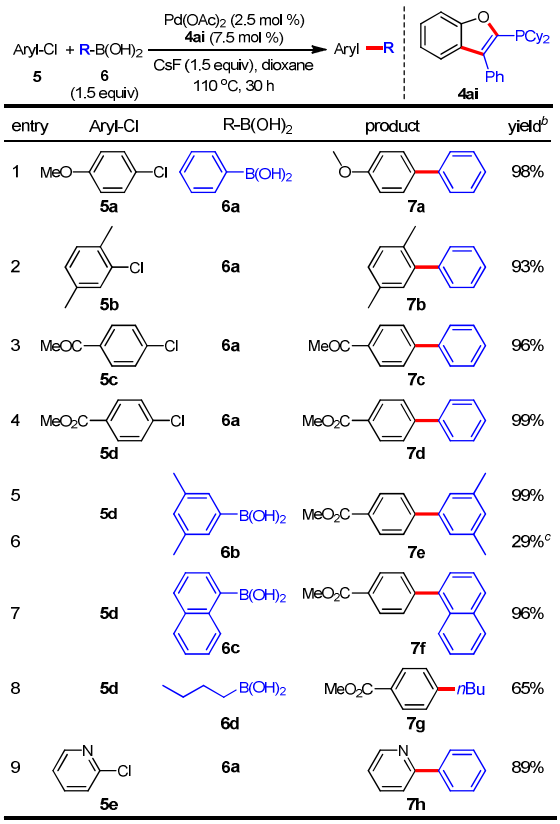
Scheme 4. Reduction of 2-Benzofuranylphosphine Sulfides and Oxides



[a]Reactions in 0.1 mmol scale (0.05 M), yields of isolated products.

With the trivalent phosphines in hand, we next turned our attention to their applications as supporting ligands in palladium-catalyzed aryl chloride transformations. As illustrated in Table 2, the combination of $Pd(OAc)_2$ and **4ai** effectively catalyzed the Suzuki-Miyaura coupling of aryl chlorides in the presence of a stoichiometric amount of CsF in dioxane.[20] Under these conditions, both electron-rich (entry 1) and electron-deficient (entries 3-7) aryl chlorides are equally efficient, and base-sensitive functional groups are well tolerant. Not surprisingly, employment of diphenylphosphino analogue, **4aa**, as ligand resulted in poor reactivity (entry 6, 29% with **4aa** *vs* entry 5, 99% with **4ai**). The chloride substrate **5b** bearing *ortho*-substituent coupled with **6a** smoothly (entry 2). Apart from functionalized arylboronic acids, preliminary experiment showed the reaction of *n*-butylboronic acid **6d** with chloride **5d** proceeded to afford the coupling product **7g** without difficulty (entry 8). Interestingly, heteroaryl chloride, such as 2-chloropyridine, was also verified to be a reactive coupling partner (entry 9).

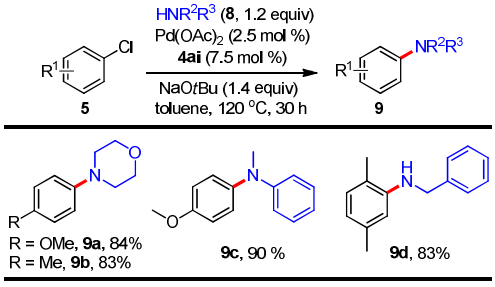
Table 2. Palladium/4ai-Catalyzed Suzuki-Miyaura Coupling of Aryl Chlorides[a]



[a]Reactions in 0.5 mmol scale (0.5 M). [b]yields of isolated products. [c]**4aa** was used instead of **4ai** as ligand.

In light of the good performance of $Pd(OAc)_2$/**4ai** in Suzuki-Miyaura couplings, this new catalytic system was further examined in Buchwald-Hartwig amination reactions (Scheme 5). Brief studies on the coupling of both electron-rich and *ortho*-substituted aryl chlorides were successful, affording **9a-d** in 83-90% yields. Meanwhile, not only secondary amines but also primary amines were readily arylated with aryl chlorides under the reaction conditions.

Scheme 5. Palladium/4ai-Catalyzed Buckwald-Hartwig Amination of Aryl Chlorides[a]



[a]Reactions in 0.5 mmol scale (1.0 M), yields of isolated products.

CONCLUSION

In summary, we have developed a step-economic way to synthesize a new class of aryl-heteroarylphosphines, 3-arylbenzofuran-2-yl phosphines, via Rh(III)-catalyzed C−H activation/annulation of *N*-phenoxyacetamides with 1-alkynylphosphine sulfides and oxides followed by reduction. This transformation proceeds in excellent regioselectivity with a broad substrate scope for both *N*-phenoxyacetamides and phosphinoacetylenes, thus allowing the heteroaromatic phosphines to have different steric and electronic properties. A combination of the air stable trivalent phosphine, 3-benzylbenzofuran-2-yl dicyclohexylphosphine **4ai**, with $Pd(OAc)_2$ provides active catalysts for both Suzuki-Miyaura coupling and Buchwald-Hartwig amination of aryl chlorides. Efforts to expand the application of this new type of aryl-heteroarylphosphine ligands are currently underway.

EXPERIMENTAL SECTION

General Procedures. All the reactions were carried out under argon atmosphere using standard Schlenk technique. ^{1}H NMR (400 MHz), ^{31}P NMR (162 MHz), ^{19}F NMR (376 MHz) and ^{13}C NMR (101 MHz) were recorded on Bruker AV400 NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra are reported in parts per million (ppm). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). HRMS were done on Agilent 6520 Q-TOF LC/MS or Varian 7.0T FTMS. $[Cp^*RhCl_2]_2$[21] and *N*-phenoxyacetamides[13a] were prepared according to the literature procedures. 1-Alkynylphosphine sulfides and oxides were prepared by treatment of the corresponding 1-alkynylphosphines with crystalline sulfur or H_2O_2.[22] 1-Alkynylphosphines were prepared by nucleophilic substitution reactions of chlorophosphines with 1-lithio-1-alkynes[22a] or Sonogashira Coupling reactions of ethynyldiphenylphosphines with iodobenzenes[22b] according to the literature procedures.

General Procedure 1: Rhodium(III)-Catalyzed C-H Activation/Annulation of *N*-phenoxyacetamides (1) with 1-alkynylphosphine derivatives (2) (Scheme 2 and 3). A mixture of **1** (0.30 mmol, 1.5 equiv), **2** (0.2 mmol), $[Cp^*Rh(MeCN)_3][SbF_6]_2$ (16.7 mg, 0.02 mmol, 10 mol %), and AgOAc (16.7 mg, 0.1 mmol, 0.5 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry DCM (2.0 mL) and HOAc (12 mg, 0.2 mmol, 1.0 equiv) was added and the resulting mixture was then put in a pre-heated oil bath at 60 °C for 20 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/EtOAc.

Diphenyl(3-phenylbenzofuran-2-yl)phosphine sulfide (3aa). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 93% yield (76.3 mg) following the general procedure 1; m.p.: 209-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.84 (m, 4H), 7.57-7.51 (m, 2H), 7.44-7.39 (m, 3H), 7.38-7.29 (m, 7H), 7.18-7.15 (m, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 156.2 (d, J = 8.7 Hz), 144.1 (d, J = 109.7 Hz), 132.0 (d, J = 11.2 Hz), 131.8 (d, J = 26.4 Hz), 131.6 (d, J = 2.8 Hz), 131.1 (d, J = 90.6 Hz), 130.3, 129.9, 128.4

(d, *J* = 8.5 Hz), 128.3, 128.0 (d, *J* = 27.9 Hz), 127.8, 126.9, 123.5, 121.4, 112.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.47; HRMS (ESI): Calcd for $C_{26}H_{20}OPS$ $[M+H]^+$ 411.0967, Found: 411.0965.

(5-Methyl-3-phenylbenzofuran-2-yl)diphenylphosph0ine sulfide (3ba). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 74% yield (62.8 mg) following the general procedure 1; m.p.: 218-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.81 (m, 4H), 7.43-7.39 (m, 3H), 7.34-7.30 (m, 7H), 7.23 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.16 (d, *J* = 2.1 Hz, 2H), 7.15 (d, *J* = 1.5 Hz, 1H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.8 (d, *J* = 8.6 Hz), 144.1 (d, *J* = 110.6 Hz), 133.2, 132.0 (d, *J* = 11.3 Hz), 131.8, 131.6, 131.2 (d, *J* = 90.1 Hz), 130.5, 129.9, 128.5 (d, *J* = 8.2 Hz), 128.3, 128.2 (d, *J* = 13.1 Hz), 127.8, 127.7, 120.9 (d, *J* = 5.3 Hz), 111.6, 21.3 (d, *J* = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.41; HRMS (ESI): Calcd for $C_{27}H_{22}OPS$ $[M+H]^+$ 425.1124, Found: 425.1124.

(5-(tert-Butyl)-3-phenylbenzofuran-2-yl)diphenylphosphine sulfide (3ca). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 72% yield (67.1 mg) following the general procedure 1; m.p.: 221-223°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.81 (m, 4H), 7.52-7.49 (m, 2H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.42-7.38 (m, 2H), 7.36-7.33 (m, 3H), 7.31 (d, *J* = 3.2 Hz, 2H), 7.30 (d, *J* = 3.2 Hz, 1H), 7.18-7.16 (m, 3H), 1.33 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.6 (d, *J* = 8.3 Hz), 146.9, 144.2 (d, *J* = 110.7 Hz), 132.3 (d, *J* = 16.1 Hz), 132.0 (d, *J* = 11.1 Hz), 131.6 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 89.9 Hz), 130.5, 129.9, 128.2 (d, *J* = 13.1 Hz), 128.0 (d, *J* = 8.3 Hz), 127.9, 127.7, 125.2, 117.0, 111.4, 34.8, 31.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.37; HRMS (ESI): Calcd for $C_{30}H_{28}OPS$ $[M+H]^+$ 467.1593, Found: 467.1617.

(5-Fluoro-3-phenylbenzofuran-2-yl)diphenylphosphine sulfide (3da). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 73% yield (62.5 mg) following the general procedure 1; m.p.: 164-166 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81(m, 4H), 7.48-7.40 (m, 3H), 7.35-7.31 (m, 6H), 7.19-7.12 (m, 5H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.6 (d, *J* = 241.1 Hz), 152.4 (d, *J* = 8.6 Hz), 146.2 (d, *J* = 108.4 Hz), 132.0 (d, *J* = 11.2 Hz), 131.9 (d, *J* = 5.2 Hz), 131.8 (d, *J* = 3.2 Hz), 130.8 (d, *J* = 90.2 Hz), 129.9, 129.7, 129.3 (dd, *J* = 10.2, 8.6 Hz), 128.3, 128.2, 128.0, 115.0 (d, *J* = 26.5 Hz), 112.9 (d, *J* = 9.5 Hz), 106.6 (d, *J* = 25.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.50; ^{19}F NMR (376 MHz, $CDCl_3$) δ -119.16; HRMS (ESI): Calcd for $C_{26}H_{19}FOPS$ $[M+H]^+$ 429.0873, Found: 429.0874.

(5-Chloro-3-phenylbenzofuran-2-yl)diphenylphosphine sulfide (3ea). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 85% yield (75.5 mg) following the general procedure 1; m.p.: 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (m, 4H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.44-7.70 (m, 3H), 7.37-7.29 (m, 7H), 7.17-7.15 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.6 (d, *J* = 8.4 Hz), 146.1 (d, *J* = 107.7 Hz), 132.1, 132.0, 131.8 (d, *J* = 3.0 Hz), 131.3 (d, *J* = 15.9 Hz), 130.8 (d, *J* = 84.5 Hz), 129.9 (d, *J* = 8.3 Hz), 129.8, 129.6 (d, *J* = 33.8 Hz), 128.3 (d, *J* = 13.3 Hz), 128.1, 128.0, 127.2, 120.9, 113.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.50; HRMS (ESI): Calcd for $C_{26}H_{19}ClOPS$ $[M+H]^+$ 445.0577, Found: 445.0579.

(5-Bromo-3-phenylbenzofuran-2-yl)diphenylphosphine sulfide (3fa). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 73% yield (71.2 mg) following the general procedure 1; m.p.: 198-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 4H), 7.65 (d, *J* = 1.5 Hz, 1H), 7.50 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.47-7.37 (m, 3H), 7.35-7.29 (m, 6H), 7.17-7.13 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.9 (d, *J* = 8.3 Hz), 145.8 (d, *J* = 107.8 Hz), 132.0 (d, *J* = 11.4 Hz), 131.8 (d, *J* = 3.0 Hz), 131.1 (d, *J* = 15.6 Hz), 130.7 (d, *J* = 90.3 Hz), 130.4 (d, *J* = 8.3 Hz), 129.9, 129.7, 129.6, 128.3 (d, *J* = 13.2 Hz), 128.1, 128.0, 124.0, 116.7, 113.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.47; HRMS (ESI): Calcd for $C_{26}H_{19}BrOPS$ $[M+H]^+$ 489.0072, Found: 489.0075.

Methyl 2-(diphenylphosphorothioyl)-3-phenylbenzofuran-5-carboxylate (3ga). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 60% yield (56.2 mg) following the general procedure 1; mp: 197-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.87-7.82 (m, 4H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.44-7.40 (m, 3H), 7.35-7.33 (m, 5H), 7.18-7.17 (m, 3H), 3.90 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.7, 158.5 (d, *J* = 8.3 Hz), 145.9 (d, *J* = 107.6 Hz), 132.2, 132.1, 132.0, 131.8 (d, *J* = 2.6 Hz), 130.6 (d, *J* = 90.4 Hz), 129.8, 129.6, 128.6 (d, *J* = 8.0 Hz), 128.3 (d, *J* = 13.2 Hz), 128.1, 128.0, 126.0, 124.0, 112.0, 52.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.50; HRMS (ESI): Calcd for $C_{28}H_{22}O_3PS$ $[M+H]^+$ 469.1022, Found: 469.1018.

Diphenyl(3-phenyl-5-(trifluoromethyl)benzofuran-2-yl)phosphine sulfide (3ha). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 63% yield (60.2 mg) following the general procedure 1; mp: 134-136 °C; ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 5H), 7.69-7.66 (m, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.45-7.41 (m, 2H), 7.36-7.31 (m, 6H), 7.21-7.16 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.3 (d, *J* = 8.5 Hz), 146.6 (d, *J* = 107.0 Hz), 132.0 (d, *J* = 11.2 Hz), 131.9 (d, *J* = 3.2 Hz), 131.8 (d, *J* = 15.6 Hz), 130.5 (d, *J* = 90.5 Hz), 129.7, 129.3, 128.6 (d, *J* = 8.5 Hz), 128.3 (d, *J* = 13.2 Hz), 128.2, 128.1, 126.4 (q, *J* = 32.2 Hz), 124.2 (d, *J* = 272.2 Hz), 123.9 (q, *J* = 3.4 Hz), 119.3 (q, *J* = 4.2 Hz), 112.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.53; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.96; HRMS (ESI): Calcd for $C_{27}H_{19}F_3OPS$ $[M+H]^+$ 479.0841, Found: 479.0848.

(6-Methyl-3-phenylbenzofuran-2-yl)diphenylphosphine sulfide (3ia). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 81% yield (68.7 mg) following the general procedure 1; mp: 183-185 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81(m, 4H), 7.43-7.39 (m, 3H), 7.35-7.26 (m, 7H), 7.16-7.11 (m, 4H), 2.48 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.7 (d, *J* = 8.1 Hz), 143.3 (d, *J* = 111.1 Hz), 137.6, 132.2, 132.1 (d, *J* = 11.2 Hz), 131.6, 131.3 (d, *J* = 90.0 Hz), 130.5, 129.9, 128.2 (d, *J* = 13.0 Hz), 127.8, 127.7, 126.1 (d, *J* = 8.4 Hz), 125.1 (d, *J* = 4.0 Hz), 120.9 (d, *J* = 3.2 Hz), 112.1 (d, *J* = 6.4 Hz), 21.8 (d, *J* = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.35; HRMS (ESI): Calcd for $C_{27}H_{22}OPS$ $[M+H]^+$ 425.1124, Found: 425.1125.

(6-Methoxy-3-phenylbenzofuran-2-yl)diphenylphosphine sulfide (3ja). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 85% yield (74.8 mg) following the general procedure 1; m.p.: 152-154 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 4H), 7.42-7.38 (m, 3H), 7.34-7.29 (m, 6H), 7.14-7.13 (m, 3H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.91 (dd, *J* = 8.7, 2.1 Hz, 1H), 3.84 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 160.0, 157.5 (d, *J* = 8.7 Hz), 142.6 (d, *J* = 112.4 Hz), 132.4 (d, *J* = 16.2 Hz), 132.0 (d, *J* = 11.3 Hz), 131.6 (d, *J* = 2.8 Hz), 131.3 (d, *J* = 90.2 Hz), 130.4, 129.8, 128.2 (d, *J* = 13.0 Hz), 127.8, 127.7, 121.7 (d, *J* = 8.5 Hz), 121.6, 113.6, 95.5, 55.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.16; HRMS (ESI): Calcd for $C_{27}H_{22}O_2PS$ $[M+H]^+$ 441.1073, Found: 441.1076.

(6-Chloro-3-phenylbenzofuran-2-yl)diphenylphosphine sulfide (3ka). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 63% yield (55.9 mg) following the general procedure 1; mp: 185-187 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 4H), 7.53 (d, *J* = 1.6 Hz, 1H), 7.46-7.40 (m, 3H), 7.36-7.30 (m, 6H), 7.28 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.17-7.15 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.1 (d, *J* =

8.5 Hz), 145.1 (d, *J* = 108.4 Hz), 132.9, 132.0 (d, *J* = 11.2 Hz), 131.8 (d, *J* = 3.0 Hz), 131.6, 130.7 (d, *J* = 90.3 Hz), 129.8, 129.7, 128.3 (d, *J* = 13.2 Hz), 128.02, 127.95, 127.1 (d, *J* = 8.3 Hz), 124.4, 122.0, 112.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.41; HRMS (ESI): Calcd for $C_{26}H_{19}ClOPS$ $[M+H]^+$ 445.0577, Found: 445.0577.

(6-Bromo-3-phenylbenzofuran-2-yl)diphenylphosphine sulfide (3la). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 73% yield (71.2 mg) following the general procedure 1; mp: 193-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.80 (m, 4H), 7.69 (s, 1H), 7.44-7.40 (m, 4H), 7.35-7.30 (m, 6H), 7.18-7.13 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.3 (d, *J* = 8.2 Hz), 145.0 (d, *J* = 108.1 Hz), 132.0 (d, *J* = 11.3 Hz), 131.8 (d, *J* = 2.8 Hz), 131.6, 130.7 (d, *J* = 90.3 Hz), 129.8, 129.7, 128.3 (d, *J* = 13.2 Hz), 128.03, 127.96, 127.5 (d, *J* = 8.5 Hz), 127.1, 122.3, 120.5, 115.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.42; HRMS (ESI): Calcd for $C_{26}H_{19}BrOPS$ $[M+H]^+$ 489.0072, Found: 489.0079.

Diphenyl(3-phenyl-6-(trifluoromethyl)benzofuran-2-yl)phosphine sulfide (3ma). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 61% yield (58.3 mg) following the general procedure 1; mp: 146-148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.80 (m, 5H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.46-7.42 (m, 2H), 7.37-7.33 (m, 6H), 7.21-7.15 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.2 (d, *J* = 8.3 Hz), 147.6 (d, *J* = 106.0 Hz), 132.1 (d, *J* = 11.2 Hz), 131.9 (d, *J* = 2.8 Hz), 131.5, 131.3 (d, *J* = 5.0 Hz), 130.7 (d, *J* = 90.4 Hz), 129.9, 129.6, 129.1 (d, *J* = 32.7 Hz), 128.4 (d, *J* = 13.3 Hz), 128.2, 128.1, 124.1 (d, *J* = 272.5 Hz), 122.1, 120.4 (d, *J* = 3.4 Hz), 109.8 (q, *J* = 4.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.57; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.41; HRMS (ESI): Calcd for $C_{27}H_{19}F_3OPS$ $[M+H]^+$ 479.0841, Found: 479.0849.

(7-Methyl-3-phenylbenzofuran-2-yl)diphenylphosphine sulfide (3na). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 78% yield (66.1 mg) following the general procedure 1; m.p.: 209-211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.84 (m, 4H), 7.43-7.31 (m, 9H), 7.23-7.19 (m, 2H), 7.18-7.15 (m, 3H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.3 (d, *J* = 8.0 Hz), 143.7 (d, *J* = 110.4 Hz), 132.2 (d, *J* = 16.2 Hz), 132.0 (d, *J* = 11.3 Hz), 131.6, 131.2 (d, *J* = 92.1 Hz), 130.6, 129.9, 128.2, 128.0, 127.81, 127.75, 127.6 (d, *J* = 19.8 Hz), 123.6, 122.2, 118.8, 14.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.46; HRMS (ESI): Calcd for $C_{27}H_{22}OPS$ $[M+H]^+$ 425.1124, Found: 425.1129.

(4,6-Dimethoxy-3-phenylbenzofuran-2-yl)diphenylphosphine sulfide (3oa). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 75% yield (70.5 mg) following the general procedure 1; mp: 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.76 (m, 4H), 7.40-7.36 (m, 2H), 7.32-7.26 (m, 6H), 7.07-7.01 (m, 3H), 6.61 (d, *J* = 1.9 Hz, 1H), 6.28 (d, *J* = 1.7 Hz, 1H), 3.82 (s, 3H), 3.62 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.0, 158.6 (d, *J* = 8.7 Hz), 155.5, 141.5 (d, *J* = 113.9 Hz), 132.4 (d, *J* = 16.6 Hz), 132.0 (d, *J* = 11.2 Hz), 131.5 (d, *J* = 90.4 Hz), 131.4 (d, *J* = 3.1 Hz), 131.0, 130.6, 128.1 (d, *J* = 13.1 Hz), 127.3, 126.8, 111.7 (d, *J* = 8.3 Hz), 95.2, 87.9, 55.7, 55.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.28; HRMS (ESI): Calcd for $C_{28}H_{24}O_3PS$ $[M+H]^+$ 471.1178, Found: 471.1177.

Diphenyl(3-(p-tolyl)benzofuran-2-yl)phosphine sulfide (3ab). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 76% yield (64.4 mg) following the general procedure 1; m.p.: 175-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.81 (m, 4H), 7.56-7.50 (m, 2H), 7.43-7.40 (m, 3H), 7.34-7.28 (m, 5H), 7.22 (d, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 7.7 Hz, 2H), 2.28 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.2 (d, *J* = 8.5 Hz), 143.8 (d, *J* = 110.2 Hz), 137.6, 132.3, 132.2 (d, *J* = 11.3 Hz), 131.5 (d, *J* = 2.6 Hz), 131.3 (d, *J* = 90.1 Hz), 129.8, 128.6, 128.5, 128.2 (d, *J* = 13.2 Hz), 127.2, 126.8, 123.4, 121.5, 112.0, 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.47; HRMS (ESI): Calcd for $C_{27}H_{22}OPS$ $[M+H]^+$ 425.1124, Found: 425.1123.

(3-(4-Methoxyphenyl)benzofuran-2-yl)diphenylphosphine sulfide (3ac). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 93% yield (81.8 mg) following the general procedure 1; m.p.: 213-215 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 4H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.43-7.39 (m, 3H), 7.35-7.27 (m, 7H), 6.68 (d, *J* = 8.6 Hz, 2H), 3.76 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.1, 156.2 (d, *J* = 8.5 Hz), 143.6 (d, *J* = 110.8 Hz), 132.1 (d, *J* = 11.2 Hz), 131.8 (d, *J* = 16.0 Hz), 131.6 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 89.6 Hz), 131.1, 128.5 (d, *J* = 8.4 Hz), 128.2 (d, *J* = 13.2 Hz), 126.8, 123.4, 122.5, 121.4, 113.4, 112.1, 55.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.37; HRMS (ESI): Calcd for $C_{27}H_{22}O_2PS$ $[M+H]^+$ 441.1073, Found: 441.1081.

(3-(4-Fluorophenyl)benzofuran-2-yl)diphenylphosphine sulfide (3ad). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 69% yield (59.2 mg) following the general procedure 1; m.p.: 180-182 °C; ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.79-7.74 (m, 4H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 6.9 Hz, 3H), 7.26-7.17 (m, 6H), 6.78-6.74 (m, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 247.6 Hz), 156.2 (d, *J* = 7.8 Hz), 144.5 (d, *J* = 109.5 Hz), 132.0 (d, *J* = 11.2 Hz), 131.7 (d, *J* = 2.5 Hz), 131.6 (d, *J* = 8.2 Hz), 131.02, 130.95 (d, *J* = 90.0 Hz), 130.9, 128.3 (d, *J* = 12.7 Hz), 127.0, 126.3 (d, *J* = 3.4 Hz), 123.6, 121.1, 114.9 (d, *J* = 21.5 Hz), 112.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.24; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.50; HRMS (ESI): Calcd for $C_{26}H_{19}FOPS$ $[M+H]^+$ 429.0873, Found: 429.0879.

(3-(4-Chlorophenyl)benzofuran-2-yl)diphenylphosphine sulfide (3ae). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 85% yield (75.5 mg) following the general procedure 1; m.p.: 194-196 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78-7.73 (m, 4H), 7.44-7.40 (m, 2H), 7.39-7.33 (m, 3H), 7.29-7.27 (m, 4H), 7.20-7.18 (m, 3H), 7.04 (d, *J* = 7.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.2 (d, *J* = 8.1 Hz), 144.8 (d, *J* = 108.8 Hz), 133.9, 132.1 (d, *J* = 11.4 Hz), 131.8 (d, *J* = 2.7 Hz), 131.22, 131.07 (d, *J* = 90.2 Hz), 130.8 (d, *J* = 15.7 Hz), 128.9, 128.4, 128.3, 128.1, 127.1, 123.7, 121.1, 112.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.27; HRMS (ESI): Calcd for $C_{26}H_{19}ClOPS$ $[M+H]^+$ 445.0577, Found: 445.0579.

(3-(4-Bromophenyl)benzofuran-2-yl)diphenylphosphine sulfide (3af). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 74% yield (72.2 mg) following the general procedure 1; m.p.: 189-191 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.80 (m, 4H), 7.52-7.43 (m, 5H), 7.36-7.33 (m, 4H), 7.28-7.26 (m, 3H), 7.20 (d, *J* = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.2 (d, *J* = 8.1 Hz), 144.7 (d, *J* = 108.9 Hz), 132.1 (d, *J* = 11.4 Hz), 131.8 (d, *J* = 2.7 Hz), 131.5, 131.05, 130.99 (d, *J* = 90.5 Hz), 130.8 (d, *J* = 15.7 Hz), 129.4, 128.4 (d, *J* = 13.2 Hz), 128.1 (d, *J* = 8.2 Hz), 127.1, 123.7, 122.2, 121.1, 112.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.29; HRMS (ESI): Calcd for $C_{26}H_{19}BrOPS$ $[M+H]^+$ 489.0072, Found: 489.0077.

Diphenyl(3-(o-tolyl)benzofuran-2-yl)phosphine sulfide (3ag). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 63% yield (53.3 mg) following the general procedure 1 but with 3.0 equiv of **1a** at 80 °C for 48 h; mp: 144-146 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.75 (m, 4H), 7.56 (d, *J* = 8.3 Hz, 1H), 7.43-7.40 (m, 3H), 7.33 (br s, 4H), 7.24-7.20 (m, 2H), 7.13-7.10 (m, 1H), 7.05-7.00 (m, 3H), 2.03 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.1 (d, *J* = 8.2 Hz), 143.9 (d, *J* = 109.9 Hz), 136.8, 132.3 (d,

J = 17.2 Hz), 132.1 (d, *J* = 4.3 Hz), 131.95 (d, *J* = 4.3 Hz), 131.69, 131.68 (d, *J* = 4.7 Hz), 131.2, 130.85, 130.83 (d, *J* = 16.5 Hz), 129.9, 129.6, 128.9 (d, *J* = 8.4 Hz), 128.28 (d, *J* = 3.0 Hz), 128.23, 128.1 (d, *J* = 3.0 Hz), 126.9, 125.3, 123.5, 121.5, 112.1, 20.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.99; HRMS (ESI): Calcd for $C_{27}H_{22}OPS$ $[M+H]^+$ 425.1124, Found: 425.1125.

(3-(naphthalen-1-yl)benzofuran-2-yl)diphenylphosphine sulfide (3ah). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 64% yield (58.9 mg) following the general procedure 1 but with 3.0 equiv of **1a** at 80 ^{o}C for 40 h; mp: 207-209 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.66 (m,7H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.48-7.45 (m, 2H), 7.38-7.37 (m, 2H), 7.34-7.28 (m, 2H), 7.26-7.16 (m, 5H), 7.06 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.3 (d, *J* = 8.6 Hz), 145.4 (d, *J* = 110.5 Hz), 133.2, 131.9 (d, *J* = 3.6 Hz), 131.8 (d, *J* = 3.5 Hz), 131.5 (d, *J* = 3.3 Hz), 131.40, 131.37, 131.34, 130.6, 130.5 (d, *J* = 1.7 Hz), 129.9 (d, *J* = 91.0 Hz), 129.5 (d, *J* = 36.1 Hz), 129.0, 128.6, 128.0 (d, *J* = 10.3 Hz), 127.8 (d, *J* = 1.4 Hz), 127.7, 127.0, 126.0, 125.9, 125.8, 125.0, 123.5, 121.8, 112.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.37; HRMS (ESI): Calcd for $C_{30}H_{22}OPS$ $[M+H]^+$ 461.1124, Found: 461.1125.

Dicyclohexyl(3-phenylbenzofuran-2-yl)phosphine sulfide (3ai). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 83% yield (70.1 mg) following the general procedure 1 but with 3.0 equiv of **1a** at 80 ^{o}C; 89% yield (753 mg) of **3ai** was isolated when the reaction was conducted in 2.0 mmol scale (0.2 M) with 3.0 equiv of **1a** at 80 ^{o}C for 30 h. m.p.: 219-221 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 1H), 7.48-7.39 (m, 7H), 7.29-7.26 (m, 1H), 2.32-2.22 (m, 2H), 2.05-2.03 (m, 2H), 1.86-1.77 (m, 4H), 1.69 (br s, 4H), 1.60-1.58 (m, 2H), 1.47-1.43 (m, 2H), 1.31-1.28 (m, 2H), 1.23-1.16 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.5 (d, *J* = 6.1 Hz), 142.4 (d, *J* = 84.6 Hz), 134.4 (d, *J* = 12.3 Hz), 130.6, 129.4 (d, *J* = 7.6 Hz), 128.2, 127.7, 126.6, 123.3, 121.3, 111.6, 38.7 (d, *J* = 52.4 Hz), 26.49, 26.45, 26.4, 26.3 (d, *J* = 6.0 Hz), 25.5 (d, *J* = 35.6 Hz) (one signal missing due to overlap); ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.42; HRMS (ESI): Calcd for $C_{26}H_{32}OPS$ $[M+H]^+$ 423.1906, Found: 423.1905.

Dicyclohexyl(5-methyl-3-phenylbenzofuran-2-yl)phosphine sulfide (3bi). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 66% yield (57.6 mg) following the general procedure 1 but with 3.0 equiv of **1a** at 80 ^{o}C; m.p.: 113-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 6H), 7.24 (d, *J* = 9.4 Hz, 1H), 7.15

(s, 1H), 2.40 (s, 3H), 2.29-2.21 (m, 2H), 2.04-2.01 (m, 2H), 1.85-1.76 (m, 4H), 1.68 (br s, 4H), 1.61-1.54 (s, 2H), 1.45-1.37 (m, 2H), 1.30-1.26 (m, 2H), 1.21-1.14 (m, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 154.0 (d, *J* = 6.3 Hz), 142.5 (d, *J* = 85.1 Hz), 134.2 (d, *J* = 12.6 Hz), 133.1, 130.8, 130.6, 129.5 (d, *J* = 7.7 Hz), 128.0 (d, *J* = 9.8 Hz), 127.7, 120.7, 111.1, 38.7 (d, *J* = 52.5 Hz), 26.51, 26.48, 26.4, 26.3 (d, *J* = 6.2 Hz), 25.6 (d, *J* = 36.3 Hz), 21.2. (one signal missing due to overlap); ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.32; HRMS (ESI): Calcd for $C_{27}H_{34}OPS$ $[M+H]^+$ 437.2063, Found: 437.2072.

(5-(tert-Butyl)-3-phenylbenzofuran-2-yl)dicyclohexylphosphine sulfide (3ci). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 90% yield (86.0 mg) following the general procedure 1 but with 3.0 equiv of **1a** at 80 ^{o}C; m.p.: 191-193 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.49 (m, 7H), 7.37-7.34 (m, 1H), 2.39-2.19 (br s, 2H), 2.16-1.98 (br s, 2H), 1.86-1.61 (m, 10H), 1.47 (br s, 2H), 1.36-1.34 (m, 11H), 1.23-1.20 (m, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 153.9, 146.7, 142.7 (d, *J* = 86.3 Hz), 134.8 (d, *J* = 13.4 Hz), 130.8, 129.1 (d, *J* = 4.9 Hz), 128.1, 127.8, 124.8, 117.0, 111.0, 38.8 (d, *J* = 52.7 Hz), 34.9, 31.8, 26.5, 26.44, 26.38, 25.6 (d, *J* = 36.1 Hz) (two signals missing due to overlap); ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.24; HRMS (ESI): Calcd for $C_{30}H_{40}OPS$ $[M+H]^+$ 479.2532, Found: 479.2537.

Dicyclohexyl(4,6-dimethoxy-3-phenylbenzofuran-2-yl)phosphine sulfide (3oi). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 75% yield (72.5 mg) following the general procedure 1 but with 3.0 equiv of **1a** at 80 ^{o}C; m.p.: 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.35 (m, 5H), 6.71 (s, 1H), 6.25 (s, 1H), 3.86 (s, 3H), 3.57 (s, 3H), 2.14-2.06 (m, 2H), 1.98-1.95 (m, 2H), 1.83-1.74 (m, 4H), 1.65 (br s, 4H), 1.56-1.53 (m, 2H), 1.45-1.42 (m, 2H), 1.25-1.21 (m, 2H), 1.18-1.24 (m, 4H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 160.7, 157.8 (d, *J* = 6.8 Hz), 155.3, 139.8 (d, *J* = 88.1 Hz), 133.2 (d, *J* = 13.1 Hz), 131.8, 130.6, 127.6, 126.8, 112.2 (d, *J* = 7.7 Hz), 94.9, 87.8, 55.6 (d, *J* = 31.0 Hz), 38.7 (d, *J* = 52.9 Hz), 26.5 (d, *J* = 3.2 Hz), 26.4, 26.3, 25.6 (d, *J* = 28.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.37; HRMS (ESI): Calcd for $C_{28}H_{36}O_3PS$ $[M+H]^+$ 483.2117, Found: 483.2112.

Diisopropyl(3-phenylbenzofuran-2-yl)phosphine sulfide (3aj). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 10/1) as a white solid in 67% yield (45.8 mg) following the general procedure 1; m.p.: 144-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.57-7.52 (m, 3H), 7.44-7.41 (m, 5H), 7.28 (d, *J* = 7.3 Hz, 1H), 2.63-2.55 (m, 2H), 1.28 (d, *J* = 6.5 Hz, 3H), 1.22 (br s, 6H), 1.17 (d, *J* = 6.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 155.5 (d, *J* = 6.1 Hz), 142.7 (d, *J* = 84.5 Hz), 134.9 (d, *J* = 12.7 Hz), 130.7, 130.5, 129.4 (d, *J* = 7.8 Hz), 128.2, 127.8, 126.8, 123.4, 121.4, 111.5, 29.4 (d, *J* = 52.9 Hz), 17.1 (d, *J* = 1.9 Hz), 15.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 59.52; HRMS (ESI): Calcd for $C_{20}H_{24}OPS$ $[M+H]^+$ 343.1280, Found: 343.1285.

Diphenyl(3-phenylbenzofuran-2-yl)phosphine oxide (3ak). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 95% yield (75.1 mg) following the general procedure 1; m.p.: 189-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.73 (m, 4H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.52-7.43 (m, 6H), 7.40-7.36 (m, 4H), 7.31 (d, *J* = 7.1 Hz, 1H), 7.27 (d, *J* = 5.2 Hz, 1H), 7.26-7.24 (m, 2H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 156.5 (d, *J* = 8.6 Hz), 144.8 (d, *J* = 128.1 Hz), 133.8 (d, *J* = 16.2 Hz), 132.0 (d, *J* = 2.6 Hz), 131.8, 131.7, 131.5 (d, *J* = 111.1 Hz), 130.1, 129.9, 128.3 (d, *J* = 12.6 Hz), 128.1, 128.0 (d, *J* = 8.7 Hz), 127.0, 123.5, 121.6, 112.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.49; HRMS (ESI): Calcd for $C_{26}H_{20}O_2P$ $[M+H]^+$ 395.1195, Found: 395.1188.

(5-Methyl-3-phenylbenzofuran-2-yl)diphenylphosphine oxide (3bk). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 98% yield (80.0 mg) following the general procedure 1; m.p.: 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.71 (m, 4H), 7.47-7.45 (m, 4H), 7.40-7.35 (m, 7H), 7.25-7.23 (m, 3H), 2.43 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 155.0 (d, *J* = 8.7 Hz), 144.8 (d, *J* = 129.0 Hz), 133.6 (d, *J* = 16.3 Hz), 133.2, 132.0 (d, *J* = 2.7 Hz), 131.8, 131.7, 131.6 (d, *J* = 111.2 Hz), 130.2, 129.9, 128.4, 128.3 (d, *J* = 12.8 Hz), 128.03, 127.95, 121.0, 111.6, 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.55; HRMS (ESI): Calcd for $C_{27}H_{22}O_2P$ $[M+H]^+$ 409.1352, Found: 409.1358.

(5-Chloro-3-phenylbenzofuran-2-yl)diphenylphosphine oxide (3ek). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 88% yield (75.3 mg) following the general procedure 1; m.p.: 132-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.71 (m, 4H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.50-7.46 (m, 2H), 7.44-7.42 (m, 3H), 7.40-7.36 (m, 5H), 7.28-7.25 (m, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 154.8 (d, *J* = 8.5 Hz), 146.7 (d, *J* = 125.7 Hz), 133.2 (d, *J* = 16.0 Hz), 132.20, 132.17, 131.8, 131.7, 131.2 (d, *J* = 111.5 Hz), 129.8, 129.4 (d, *J* = 5.8 Hz), 128.5, 128.3, 128.2, 127.3, 121.1, 113.2; ^{31}P NMR (162 MHz,

$CDCl_3$) δ 17.30; HRMS (ESI): Calcd for $C_{26}H_{19}ClO_2P$ $[M+H]^+$ 429.0806, Found: 429.0811.

Dicyclohexyl(3-phenylbenzofuran-2-yl)phosphine oxide (3al). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 2/1) as a white solid in 98% yield (79.8 mg) following the general procedure 1 at 80 ^oC; m.p.: 139-141 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65-7.56 (m, 4H), 7.47-7.37 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 1H), 2.17-2.08 (m, 2H), 2.02-1.99 (m, 2H), 1.82-1.66 (m, 8H), 1.54-1.36 (m, 4H), 1.31-1.14 (m,6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.0 (d, *J* = 6.9 Hz), 143.8 (d, *J* = 103.2 Hz), 134.7 (d, *J* = 11.4 Hz), 130.2, 130.1, 128.2 (d, *J* = 7.4 Hz), 128.1, 127.9, 126.4, 123.3, 121.4, 111.7, 36.2 (d, *J* = 69.9 Hz), 26.3 (d, *J* = 9.0 Hz), 26.2 (d, *J* = 8.8 Hz), 25.7, 25.4 (d, *J* = 2.8 Hz), 24.5 (d, *J* = 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.23; HRMS (ESI): Calcd for $C_{26}H_{32}O_2P$ $[M+H]^+$ 407.2134, Found: 407.2132.

General Procedure 2: $(Me_3Si)_3SiH$-Mediated Radical Desulfidation Reaction (Scheme 4a). A mixture of **3** (0.1 mmol, 1.0 equiv), AIBN (1.64 mg, 0.01 mmol, 10 mol %) were weighted in a Schlenk tube equipped with a stir bar. Dry toluene (2.0 mL) and $(Me_3Si)_3SiH$ (0.15 mmol, 1.5 equiv, 37.3mg) were added and the resulting mixture was then put in a pre-heated oil bath at 80 °C for 12 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether.

General Procedure 4: Deoxidation of Phosphine Oxides to Trivalent Phosphines (Scheme 4b). A mixture of **3** (0.1 mmol, 1.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry xylene (2.0 mL), $HSiCl_3$ (0.83 mmol, 8.3 equiv, 112.4mg) and Et_3N (611.7 mg, 3.3 mmol, 33 equiv) was added and the resulting mixture was then put in a pre-heated oil bath at 150 °C for 48 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether.

Diphenyl(3-phenylbenzofuran-2-yl)phosphine (4aa). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 99% yield (37.4 mg) following the general procedure 2 and 99% yield (37.4 mg) following the general procedure 3, respectively; m.p.: 168-170 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J*

= 7.2 Hz, 2H), 7.43-7.41 (m, 7H), 7.36-7.32 (m, 1H), 7.26 (br s, 7H), 7.20-7.15 (m, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 157.4, 150.4 (d, *J* = 36.3 Hz), 135.9 (d, *J* = 6.2 Hz), 133.9 (d, *J* = 28.2 Hz), 133.6 (d, *J* = 19.7 Hz), 131.9 (d, *J* = 1.4 Hz), 130.0 (d, *J* = 3.7 Hz), 128.8, 128.5, 128.4, 128.0 (d, *J* = 6.4 Hz), 127.9, 125.7, 122.9, 120.7, 111.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ -30.65; HRMS (ESI): Calcd for $C_{26}H_{20}OP$ $[M+H]^+$ 379.1246, Found: 379.1253.

(5-(tert-butyl)-3-phenylbenzofuran-2-yl)diphenylphosphine (4ca). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 99% yield (43.0 mg) following the general procedure 2; m.p.: 177-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.54-7.51 (m, 6H), 7.47-7.42 (m, 3H), 7.35 (br s, 6H), 1.38 (s, 9H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 155.7, 150.6 (d, *J* = 35.9 Hz), 146.1, 136.0 (d, *J* = 5.9 Hz), 134.2 (d, *J* = 27.8 Hz), 133.5 (d, *J* = 19.6 Hz), 132.1, 130.0 (d, *J* = 3.8 Hz), 128.7, 128.5 (d, *J* = 7.4 Hz), 128.4, 127.8, 127.6 (d, *J* = 6.2 Hz), 123.8, 116.6, 111.2, 34.8, 31.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ -30.59; HRMS (ESI): Calcd for $C_{30}H_{28}OP$ $[M+H]^+$ 435.1872, Found: 435.1886.

(5-chloro-3-phenylbenzofuran-2-yl)diphenylphosphine (4ea). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 99% yield (40.8 mg) following the general procedure 2; m.p.: 134-136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.40-7.37 (m, 6H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.29 (d, *J* = 6.5 Hz, 1H), 7.26-7.23 (m, 6H), 7.18 (dd, *J* = 8.8, 2.0 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 155.7, 152.3 (d, *J* = 38.9 Hz), 135.5 (d, *J* = 6.0 Hz), 133.7, 133.5, 133.3 (d, *J* = 27.8 Hz), 131.2 (d, *J* = 1.9 Hz), 129.8 (d, *J* = 3.6 Hz), 129.4 (d, *J* = 6.0 Hz), 128.9, 128.6 (d, *J* = 7.8 Hz), 128.5, 128.2, 125.9, 120.3, 112.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ -30.37; HRMS (ESI): Calcd for $C_{26}H_{19}ClOP$ $[M+H]^+$ 413.0857, Found: 413.0866.

Dicyclohexyl(3-phenylbenzofuran-2-yl)phosphine (4ai). The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 99% yield (38.6 mg) following the general procedure 2 and 99% yield (38.6 mg) following the general procedure 3, respectively; m.p.: 165-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 4H), 7.49-7.45 (m, 2H), 7.40-7.35 (m, 2H), 7.28-7.24 (m, 1H), 2.23-2.18 (m, 2H), 1.86-1.83 (m, 2H), 1.77-1.74 (m, 2H), 1.67-1.60 (m, 6H), 1.38-1.31 (m, 2H), 1.28-1.15 (m, 8H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 156.9, 152.9 (d, *J* = 44.6 Hz), 134.2 (d, *J* = 23.0 Hz), 132.5, 130.1 (d, *J* = 3.1 Hz), 128.3, 127.4, 125.0, 122.5, 120.4, 111.4, 33.4 (d, *J* = 8.5 Hz), 30.6 (d, *J* = 17.2 Hz), 30.0 (d, *J* = 6.7 Hz), 27.2 (d,

J = 5.5 Hz), 27.1, 26.4 (one signal missing due to overlap); ^{31}P NMR (162 MHz, $CDCl_3$) δ -22.78; HRMS (ESI): Calcd for $C_{26}H_{32}OP$ $[M+H]^+$ 391.2185, Found: 391.2195.

General Procedure 4: Suzuki-Miyaura Cross-Coupling Reactions using 4ai as Ligand (Table 2). A mixture of boronoic acid **6** (0.75 mmol, 1.5 equiv), **4ai** (14.6 mg, 0.0375 mmol, 7.5 mol %), $Pd(OAc)_2$ (2.81 mg, 0.0125 mmol, 2.5 mol %), CsF (227.9 mg, 1.5 mmol, 3.0 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry dioxane (1.0 mL) and aryl chloride **5** (0.5 mmol, 1.0 equiv) was added and the resulting mixture was then put in a pre-heated oil bath at 110 °C for 30 h under vigorous stirring. The reaction was cooled to room temperature and transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/EtOAc.

4-Methoxy-1,1'-biphenyl (7a).[1d] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 98% yield (90.7 mg) following the general procedure 4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, J = 8.3 Hz, 4H), 7.43 (t, J = 7.7 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.

2,5-Dimethyl-1,1'-biphenyl (7b).[23] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 93% yield (84.6 mg) following the general procedure 4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (m, 2H), 7.44 (m, 3H), 7.28 (d, J = 8.3 Hz, 1H), 7.20 (d, J = 6.5 Hz, 2H), 2.47 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.0, 141.7, 135.1, 132.1, 130.5, 130.2, 129.1, 128.0, 127.9, 126.6, 20.9, 19.9.

1-([1,1'-Biphenyl]-4-yl)ethanone (7c).[24] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 96% yield (94.1 mg) following the general procedure 4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 7.1 Hz, 2H), 7.48 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 2.65 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.7, 145.7, 139.8, 135.8, 128.92, 128.88, 128.2, 127.23, 127.18, 26.6.

Methyl [1,1'-biphenyl]-4-carboxylate (7d).[1d] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 99% yield (104.9 mg) following the general procedure 4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.5 Hz,

2H), 7.65-7.61 (m, 2H), 7.47 (t, J = 7.4 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 3.95 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.9, 145.6, 139.9, 130.0, 128.9, 128.8, 128.1, 127.2, 127.0, 52.1.

Methyl 3',5'-dimethyl-[1,1'-biphenyl]-4-carboxylate (7e).[25] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 99% yield (119.8 mg) following the general procedure 4; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.6 Hz, 2H), 7.25 (s, 2H), 7.05 (s, 1H), 3.94 (s, 3H), 2.40 (s, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.0, 145.8, 139.9, 138.4, 129.9, 129.7, 128.6, 127.0, 125.1, 52.0, 21.3.

Methyl 4-(naphthalen-1-yl)benzoate (7f).[26] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 96% yield (126.3 mg) following the general procedure 4; ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 2H), 7.94-7.89 (m, 2H), 7.85 (d, J = 8.5 Hz, 1H), 7.59 (d, J = 8.4 Hz, 2H), 7.56-7.54 (m, 1H), 7.53-7.50 (m, 1H), 7.47-7.42 (m, 2H), 3.98 (s,3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.0, 145.6, 139.1, 133.7, 131.2, 130.1, 129.6, 129.0, 128.4, 128.2, 126.9, 126.3, 126.0, 125.6, 125.3, 52.2.

Methyl 4-butylbenzoate (7g).[27] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as a white solid in 65% yield (62.4 mg) following the general procedure 4; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 3.90 (s, 3H), 2.66 (t, J = 7.7 Hz, 2H), 1.65-1.57 (m, 2H), 1.40-1.30 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 167.2, 148.5, 130.9, 129.6, 128.7, 128.4, 127.6, 51.9, 35.7, 33.24, 22.3, 13.9.

2-Phenylpyridine (7h).[24] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether) as an oil in 89% yield (69 mg) following the general procedure 4; ^1H NMR (400 MHz, $CDCl_3$) δ 8.71-8.69 (m, 1H), 8.01-8.00 (m, 1H), 7.99-7.96 (m, 1H), 7.75-7.72 (m, 2H), 7.50-7.47 (m, 2H), 7.44-7.40 (m, 1H), 7.25-7.21 (m, 1H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.4, 149.6, 139.3, 136.8, 128.9, 128.7, 126.9, 122.1, 120.6.

General Procedure 5: Buchwald–Hartwig Cross-Coupling Reactions using 4ai as Ligand (Scheme 5). A mixture of **4ai** (14.6 mg, 0.0375 mmol, 7.5 mol %), $Pd(OAc)_2$ (2.81 mg, 0.0125 mmol, 2.5 mol %), NaO*t*Bu (67.3 mg, 0.7 mmol, 1.4 equiv) were weighted in a Schlenk tube equipped with a stir bar. Dry toluene (0.5 mL), aryl chloride **5** (0.5 mmol, 1.0 equiv) and amine **8** (0.6 mmol, 1.2 equiv) was added and the resulting mixture was then put in a pre-heated oil bath at 120 °C for 30 h under vigorous stirring. The reaction was cooled to room temperature and

transferred to a 100 mL round-bottomed flask using CH_2Cl_2. Silica was added to the flask and volatiles were evaporated under reduced pressure. The purification was performed by flash column chromatography on silica gel with petroleum ether/EtOAc.

4-(4-methoxyphenyl)morpholine (9a).[1d] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 100/1) as a white solid in 84% yield (80.6 mg) following the general procedure 5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (t, *J* = 10.3 Hz, 4H), 3.87 (t, *J* = 4.5 Hz, 4H), 3.77 (s, 3H), 3.07 (s, *J* = 4.5 Hz, 4H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.0, 145.4, 117.8, 114.4, 66.9, 55.5, 50.8.

4-(p-tolyl)morpholine (9b).[1e] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 100/1) as a white solid in 83% yield (73.2 mg) following the general procedure 5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 3.99-3.75 (m, 4H), 3.27-2.91 (m, 4H), 2.29 (s,3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 149.1, 129.7, 129.6, 116.0, 66.9, 49.9, 20.4.

4-methoxy-N-methyl-N-phenylaniline (9c).[1d] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 100/1) as a tan solid in 90% yield (95.9 mg) following the general procedure 5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 9.0, 7.1 Hz, 2H), 7.16-7.14 (m, 2H), 6.95-6.93 (m, 2H), 6.86-6.84 (m, 3H), 3.86 (s, 3H), 3.31 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.3), 149.6, 142.1, 128.9, 126.2, 118.4, 115.7, 114.7, 55.5, 40.5.

N-benzyl-2,5-dimethylaniline (9d).[1e] The title compound was isolated by silica gel column chromatography (eluent: Petroleum ether/EtOAc= 100/1) as a colorless oil in 83% yield (87.1 mg) following the general procedure 5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36(m, 4H), 7.33-7.29 (m, 1H), 6.98(d, *J* =2.0, 1H), 6.55-6.50 (m, 2H), 4.38 (s, 2H), 3.93 (br, 1H), 2.29 (s, 3H), 2.14 (s, 3H); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 145.9, 139.5, 136.8, 129.9, 128.6), 127.7, 127.2, 119.0, 117.9, 110.9, 48.4, 21.5, 17.1.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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Supporting information

Additional experimental data, analytical data, and ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra for all new compounds (PDF); and crystallographic data for compounds **3aa, 3ja, 3ka, 3ai, 3ak**, and **4ai** (CIF). This material is available free of charge e on the ACS Publications website.

REFERENCES

(1) For reviews, see: (a) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.* **2008**, *41*, 1461-1473. (b) Surry, D. S.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2008**, *47*, 6338-6361. (c) Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 27–50. For initial reports, see: (d) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722-9723. (e) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **1999**, *38*, 2413-2416.

(2) (a) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685-4686. (b) Walker, S. D.; Barder, T.; Martinelli, E. J. R.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2004**, *43*, 1871-1876. (c) Yin, J. J.; Rainka, M. P.; Zhang, X. X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162-1163. (d) Christmann, U.; Vilar, R.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2004**, 1294-1295. (e) Christmann, U.; Pantazis, D. A.; Benet-Buchholz, J.; McGrady, J. E.; Maseras,

F.; Vilar, R. *J. Am. Chem. Soc.* **2006**, *128*, 6376-6390. (f) Barder, T. E. *J. Am. Chem. Soc.* **2006**, *128*, 898-904. (g) Reid, S. M.; Boyle, R. C.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 7816-7817. (h) Yamashita, M.; Takamiya, I.; Jin, K.; Nozaki, K. J. *Organomet. Chem.* **2006**, *691*, 3189-3195.

(3) (a) Barder, T. E.; Biscoe, M. R.; Buchwald, S. L. *Organometallics* **2007**, *26*, 2183-2192. (b) Barder, T. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 12003-12010.

(4) For selected reviews, see: (a) Andersen, N. G.; Keay, B. *A. Chem. Rev.* **2001**, *101*, 997-1030. (b) Au-Yeung, T. T. L.; Chan, A. S. C. *Coord. Chem. Rev.* **2004**, *248*, 2151-2164. (c) Grotjahn, D. B. *Dalton Trans.* **2008**, *46*, 6497–6508. (d) Wong, M. W.; So, C. M.; Kwong, F. Y. *Synlett* **2012**, *23*, 1132-1153. (e) Wong, S. M.; Yuen, O. Y.; Choy, P. Y.; Kwong, F. Y. *Coord. Chem. Rev.* **2015**, *293-294*, 158-186.

(5) For selected examples, see: (a) Harkal, S.; Rataboul, F.; Zapf, A.; Fuhrmann, C.; Riermeier, T.; Monsees, A.; Beller, M. *Adv. Synth. Catal.* **2004**, *346*, 1742-1748. (b) Schulz, T.; Torborg, C.; Schäffner, B.; Huang, J.; Zapf, A.; Kadyrov, R.; Börner, A.; Beller, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 918-921. (c) Hu, T.; Schulz, T.; Torborg, C.; Chen, X.; Wang, J.; Beller, M.; Huang, J. *Chem. Commun.* **2009**, 7330-7332. (d) Seacome, R. J.; Coles, M. P.; Glover, J. E.; Hitchcock, P. B.; Rowlands, G. J. *Dalton Trans.* **2010**, *39*, 3687-3694. (e) Milde, B.; Schaarschmidt, D.; Rüffer, T.; Lang, H. *Dalton Trans.* **2012**, *41*, 5377-5390. (f) Fleischer, I.; Dyballa, K. M.; Jennerjahn, R.; Jackstell, R.; Franke, R.; Spannenberg, A.; Beller, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 2949-2953. (g) Austeri, M.; Enders, M.; Nieger, M.; Bräse, S. Eur. *J. Org. Chem.* **2013**, 1667-1670. (h) Wu, L.; Fleischer, I.; Jackstell, R.; Beller, M. *J. Am. Chem. Soc.* **2013**, *135*, 3989-3996. (i) Liu, J.; Kubis, C.; Franke, R.; Jackstell, R.; Beller, M. *ACS Catal.* **2016**, *6*, 907-912.

(6) Zapf, A.; Jackstell, R.; Rataboul, F.; Riermeier, T.; Monsees, A.; Fuhrmann, C.; Shaikh, N.; Dingerdissenb, U.; Beller, M. *Chem. Commun.* **2004**, 38-39.

(7) (a) Liu, D.; Gao, W.; Dai, Q.; Zhang, X. *Org. Lett.* **2005**, *7*, 4907-4910. (b) Dai, Q.; Gao, W.; Liu, D.; Kapes, L. M.; Zhang, X. *J. Org. Chem.* **2006**, *71*, 3928-3934. (c) Zink, D. M.; Baumann, T.; Nieger, M.; Bräse, S. Eur. *J. Org. Chem.* **2011**, 1432-1437.

(8) For selected examples, see: (a) So, C. M.; Lau, C. P.; Kwong, F. Y. *Org. Lett.* **2007**, *9*, 2795-2798. (b) Lee, H. W.; Lam, F. L.; So, C. M.; Lau, C. P.; Chan, A. S. C.; Kwong, F. Y. *Angew. Chem. Int. Ed.* **2009**, *48*, 7436-7439. (c) Kondoh, A.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2010**, *12*,

1476-1479. (d) So, C. M.; Chow, W. K.; Choy, P. Y.; Lau, C. P.; Kwong, F. Y. *Chem. - Eur. J.* **2010**, *16*, 7996-8001. (e) Chow, W. K.; Yuen, O. Y.; So, C. M.; Wong, W. T.; Kwong, F. Y. *J. Org. Chem.* **2012**, *77*, 3543-3548. (f) Jia, T.; Bellomo, A.; Baina, K. EL; Dreher, S. D.; Walsh, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 3740-3743. (g) Zheng, B.; Jia, T.; Walsh, P.J. *Org. Lett.* **2013**, *15*, 4190-4193. (h) Yuen, O. Y.; So, C. M.; Man, H. W.; Kwong, F. Y. *Chem. Eur. J.* **2016**, *22*, 6471-6476.

(9) Li, B.; Yang, J.; Xu, H.; Song, H.; Wang, B. *J. Org. Chem.* **2015**, *80*, 12397-12409.

(10) For selected examples of phosphines containing benzofuran-2-yl group, see: (a) Sannicolò, F.; Benincori, T.; Rizzo, S.; Gladiali, S.; Pulacchini, S.; Zottid, G. *Synthesis* **2001**, 2327-2336. (b) Artemova, N. V.; Chevykalova, M. N.; Luzikov, Y. N.; Nifant'ev, I. E.; Nifant'ev, E. E. *Tetrahedron* **2004**, *60*, 10365-10370.

(11) For recent reviews on Rh (III)-catalyzed C- H activation, see: (a) Satoh, T.; Miura, M. *Chem. Eur. J.* **2010**, *16*, 11212-11222. (b) Patureau, F. W.; Wencel-Delord, J.; Glorius, F. *Aldrichim. Acta* **2012**, *45*, 31-41. (c) Chiba, S. *Chem. Lett.* **2012**, *41*, 1554-1559. (d) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651-3678. (e) Kuhl, N.; Schröder, N.; Glorius, F. *Adv. Synth. Catal.* **2014**, *356*, 1443-1460. (f) Song, G.; Li, X. *Acc. Chem. Res.* **2015**, *48*, 1007-1020. (g) Ye, B.; Cramer, N. *Acc. Chem. Res.* **2015**, *48*, 1308-1318. (h) Gulías, M.; Mascareñas, J. L. *Angew. Chem. Int. Ed.* **2016**, *55*, 11000-11019.

(12) (a) Li, B.; Feng, H.; Xu, S.; Wang, B. *Chem. Eur. J.* **2011**, *17*, 12573-12577. (b) Tan, X.; Liu, B.; Li, X.; Li, B.; Xu, S.; Song, H.; Wang, B. *J. Am. Chem. Soc.* **2012**, *134*, 16163-16166. (c) Li, B.; Feng, H.; Wang, N.; Ma, J.; Song, H.; Xu, S.; Wang, B. *Chem.-Eur. J.* **2012**, *18*, 12873-12879. (d) Li, B.; Wang, N.; Liang, Y.; Xu, S.; Wang, B. *Org. Lett*. **2013**, *15*, 136-139. (e) Li, B.; Xu, H.; Wang, H.; Wang, B. *ACS Catal.* **2016**, *6*, 3856-3862. (f) Ge, Q.; Hu, Y.; Li, B.; Wang, B. *Org. Lett*. **2016**, *18*, 2483-2486.

(13) For selected examples on metal-catalyzed redox-neutral C-H activation of *N*-phenoxyacetamides, see: (a) Liu, G.; Shen, Y.; Zhou, Z.; Lu, X. *Angew. Chem. Int. Ed.* **2013**, *52*, 6033-6037. (b) Hu, F.; Xia, Y.; Ye, F.; Liu, Z.; Ma, C.; Zhang, Y.; Wang, J. *Angew. Chem. Int. Ed.* **2014**, *53*, 1364-1367. (c) Zhou, J.; Shi, J.; Qi, Z.; Li, X.; Xu, H. E.; Yi, W. *ACS Catal.* **2015**, *5*, 6999-7003. (d) Li, B.; Lan, J.; Wu, D.; You, J. *Angew. Chem. Int. Ed.* **2015**, *54*, 14008-14012. (e) Wang, X.; Lerchen, A.; Gensch, T.; Knecht, T.; Daniliuc, C. G.; Glorius, F. *Angew. Chem. Int. Ed.* **2017**, *56*, 1381-1384. (f) Wang, X.; Gensch, T.; Lerchen, A.; Daniliuc, C. G.; Glorius, F. *J. Am.*

Chem. Soc. **2017**, *139*, 6506-6512. (g) Wu, Q.; Chen, Y.; Yan, D.; Zhang, M.; Lu, Y.; Sun, W.-Y.; Zhao, J. *Chem. Sci.* **2017**, *8*, 169-173 and references cited therein.

(14) For review on 1-alkynylphosphines and their derivatives for new phosphines synthesis, see: (a) Kondoh, A.; Yorimitsu, H.; Oshima, K. *Chem. Asian J.* **2010**, *5*, 398-409. For selected examples, see: (b) Kondoh, A.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 6996-6997. (c) Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 3951-3954. (d) Heller, B.; Gutnov, A.; Fischer, C.; Drexler, H.-J.; Spannenberg, A.; Redkin, D.; Sundermann, C.; Sundermann, B. *Chem. - Eur. J.* **2007**, *13*, 1117-1128. (e) Schelper, M.; Buisine, O.; Kozhushkov, S.; Aubert, C.; de Meijere, A.; Malacria, M. *Eur. J. Org. Chem.* **2005**, 3000-3007. (f) Slowinski, F.; Aubert, C.; Malacria, M. *J. Org. Chem.* **2003**, *68*, 378-386. (g) Doherty, S.; Knight, J. G.; Smyth, C. H.; Harrington, R. W.; Clegg, W. *Org. Lett.* **2007**, *9*, 4925-4928. (h) Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem. Int. Ed.* **2008**, *47*, 3410-3413.

(15) CCDC 1545538 (**3aa**), 1545540 (**3ka**), 1545542 (**3ja**), 1545543 (**3ak**), 1545544 (**3ai**) and 1545545 (**4ai**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(16) Simmons, E. M.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2012**, *51*, 3066-3072.

(17) A tentative mechanism is proposed, see the Supporting Information for details.

(18) Romeo, R.; Wozniak, L. A.; Chatgilialoglu, C. *Tetrahedron Lett.* **2000**, *41*, 9899-9902.

(19) Doherty, S.; Smyth, C. H.; Harrington, R. W.; Clegg, W. *Organometallics* **2009**, *28*, 5273-5276.

(20) When the coupling reaction of **5a** with **6a** was conducted with 1.0 mol % of $Pd(OAc)_2$, **7a** was isolated in 32% yield.

(21) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228-234.

(22) (a) Kondoh, A.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 4099-4104. (b) Peng, L.; Xu, F.; Suzuma, Y.; Orita, A.; Otera, J. *J. Org. Chem.* **2013***, 78,* 12802-12808.

(23) Yang, S.-D.; Sun, C.-L.; Fang, Z.; Li, B.-J.; Li, Y.-Z.; Shi, Z.-J. *Angew. Chem. Int. Ed.* **2008***, 47,* 1473-1476.

(24) So, C. M.; Yeung, C. C.; Lau, C. P.; Kwong, F. Y. *J. Org. Chem.* **2008**, *73*, 7803–7806.

(25) Guan, B.-T.; Wang, Y.; Li, B.-J.; Yu, D.-G.; Shi, Z.-J.; *J. Am. Chem. Soc.* **2008**, *130*, 14468–

14470.

(26) Leowanawat, P.; Zhang, N.; Percec, V. *J. Org. Chem.* **2012**, *77*, 1018−1025.

(27) Kondolff, I.; Doucet, H.; Santell, M. *Organometallics* **2006**, *25*, 5219−5222.