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Palladium-Catalyzed C−P(III) Bond Formation by Coupling ArBr/ArOTf with Acylphosphines

Xingyu Chen, Hongyu Wu, Rongrong Yu, Hong Zhu,* and Zhiqian Wang*

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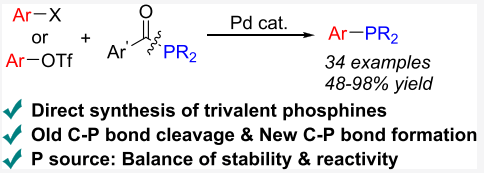
ABSTRACT: Palladium-catalyzed C−P bond formation reaction of ArBr/ArOTf using acylphosphines as differential phosphination reagents is reported. The acylphosphines show practicable reactivity with ArBr and ArOTf as the phosphination reagents, though they are inert to the air and moisture. The reaction affords trivalent phosphines directly in good yields with a broad substrate scope and functional group tolerance. This reaction discloses the acylphosphines' capability as new phosphorus sources for the direct synthesis of trivalent phosphines.

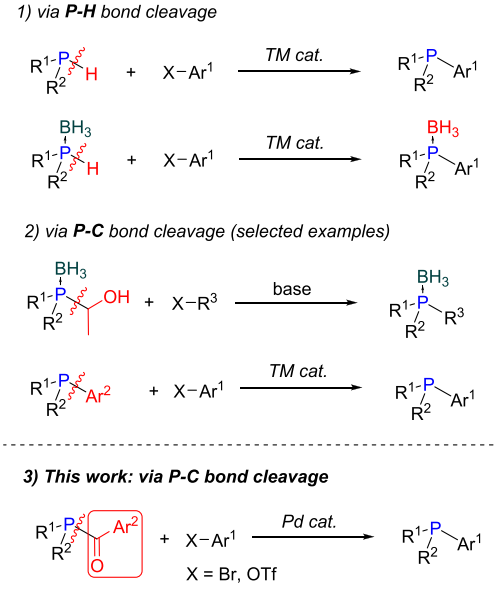


INTRODUCTION

Transition-metal (TM)-catalyzed C−P bond formation reactions are playing notable roles in the synthesis of trivalent phosphines, which are widely used in metal complexes, catalysts, materials, medicinal compounds, and organic reagents.[1] In these reactions, organophosphorus compounds are usually employed as nucleophilic partners to achieve the phosphination of various coupling substrates.[2] Comparing to the great diversity of coupling substrates, the studies on extending the phosphination reagents are rarely reported.[3] In principle, secondary phosphines or their metal salts are formally original phosphination reagents for coupling reactions (Scheme 1, 1). However, their applications are very limited for their relatively low reactivity and catalyst poisoning.[4] To some extent, this fact makes the indirect synthesis of trivalent phosphines through the formation of phosphine oxides and consequent reduction become a more favored option.[5] Notably, the phosphine-borane complexes conquered these drawbacks and become welcomed in the direct synthesis of phosphines.[6] The introduction of borane group not only significantly enhances the phosphination reagents' reactivity but also stabilizes both the starting material and the target product.

Nowadays, some trivalent phosphines have emerged as a new type of phosphination reagents via a C−P bond cleavage process (Schemes 1, 2).[7] For example, hydroxymethylphosphine derivatives are used as "masked secondary phosphines" in several novel C−P bond formation reactions developed by Hayashi, Herault, and Buono, respectively. Furthermore, triarylphosphines can also be used as phosphination reagents through a TM-catalyzed aryl group exchanging process.[8] The trivalent phosphines usually have higher stability than secondary phosphines but suffer from relatively lower reactivity as phosphination reagents. Inspired by this challenge, we hope to develop a new phosphination reagent, which has good stability for easy bench operating and high reactivity for phosphine synthesis directly and efficiently. Acylphosphines, prepared from acyl chlorides and secondary phosphines, usually are more stable than secondary phosphines to the air and moisture. In this work, we report a palladium-catalyzed C−P bond formation reaction of ArBr/ArOTf using

Scheme 1. Outlines of TM-Catalyzed Direct Synthesis of Phosphines



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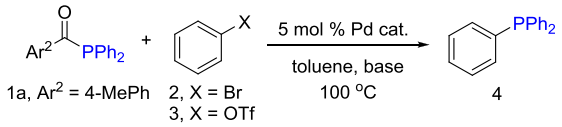
acylphosphines as differential phosphination reagents, which show practicable reactivity (Scheme 1, 3).

RESULTS AND DISCUSSIONS

The feasibility of C−P bond coupling using acylphosphines was disclosed in a previous work,[9] but the substrate scope was limited to aryl iodides and alkyl bromides because of their relatively low reactivity. With PhBr **2** as the coupling partner and $Pd(OAc)_2$ as the catalyst, trivalent phosphine product **4** is afforded in merely 14% yield (Table 1, entry 1). The use of

Table 1. Optimization of Reaction Conditions[d]



entry	X	catalyst	base	yield (%)
1	Br	$Pd(OAc)_2$/-	Cs_2CO_3	14
2	Br	$Pd_2(dba)_3$/-	Cs_2CO_3	22
3	Br	$Pd_2(dba)_3/PCy_3$	Cs_2CO_3	38
4	Br	$Pd_2(dba)_3$/dppe	Cs_2CO_3	55
5	Br	$Pd_2(dba)_3$/dppp	Cs_2CO_3	73
6	Br	$Pd_2(dba)_3$/dppf	Cs_2CO_3	96(94[a])
7	Br	$Pd(OAc)_2$/dppf	Cs_2CO_3	63
8	Br	$PdCl_2$(dppf)	Cs_2CO_3	39
9	Br	$Pd_2(dba)_3$/dppf	Cs_2CO_3	50[b]
10	Br	$Pd_2(dba)_3$/dppf	Na_2CO_3	57
11	Br	$Pd_2(dba)_3$/dppf	K_3PO_4	71
12	Br	$Pd_2(dba)_3$/dppf	Et_3N	6
13	Br	$Pd_2(dba)_3$/dppf	Cs_2CO_3	77[c]
14	OTf	$Pd_2(dba)_3$/dppf	Cs_2CO_3	30
15	OTf	$Pd_2(dba)_3$/dppp	Cs_2CO_3	55
16	OTf	$PdCl_2$(dppp)	Cs_2CO_3	99(98[a])
17	OTf	$PdCl_2(PhCN)_2$/dppp	Cs_2CO_3	95

[a]Isolated yield. [b]Under 80 °C. [c]1,4-dioxane as a solvent. [d]Reaction conditions: **1** (0.2 mmol), **2** or **3** (0.21 mmol), toluene (0.5 mL), base (0.22 mmol), catalyst (5 mol % Pd), in N_2, under 100 °C for 12 h; yield determined by ^{31}P NMR.

palladium (0) catalyst and electron-rich phosphine ligands is found to be efficient to enhance the yield (Table 1, entries 2 and 3). The bidentate ligands, such as dppf, significantly improve the conversion and afford triphenylphosphine **4** in a yield of 96% (Table 1, entries 4−6). As to the catalyst, Pd(0) precursor $Pd_2(dba)_3$ is more effective than Pd(II) complexes. Comparing to a 96% yield achieved by $Pd_2(dba)_3$, the yield drops to a moderate level using Pd(II) complexes even with the same ligand dppf (Table 1, entries 7 and 8). In further optimization, the temperature of 100 °C is necessary to gain a high yield. The lower temperature, such as 80 °C, leads to a longer reacting time and a drop of yield (Table 1, entry 9). Exploring the scope of bases demonstrates the inorganic bases are more helpful than the organic bases, and Cs_2CO_3 is found to be the best one (Table 1, entries 10−12). Varying the solvent reveals that nonpolar solvents are better than polar aprotic solvents, and 77% yield can be achieved in 1,4-dioxane (Table 1, entry 13), but in very low yield in DMF or DMSO (not shown).

The process of this reaction is observed by monitoring the ^{31}P NMR yields of PPh_3 from small potions taken from the reaction mixture at a certain time (as shown in Figure 1). The

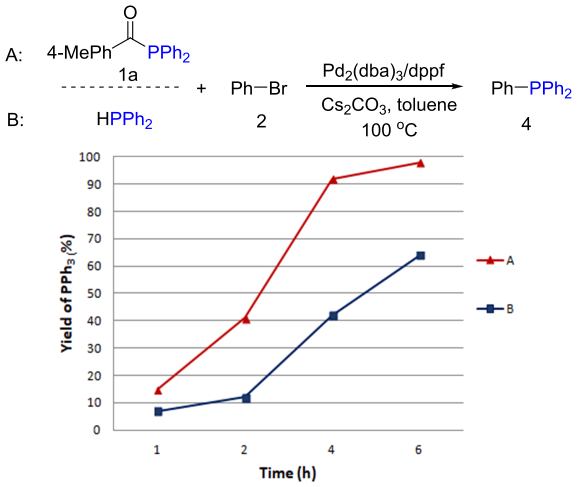


Figure 1. Reaction Process: Acylphosphine vs HPPh2.

acylphosphine **1a** is highly reactive under the optimized condition (Table 1, entry 6), even higher than the secondary phosphine $HPPh_2$. The yield of PPh_3 in reaction **A** reaches to 92% in 4 h and 98% in 6 h. In the same condition, employing $HPPh_2$ as the phosphination reagent, only 42% yield is afforded in 4 h (Figure 1, reaction **B**).

When the aryl triflate PhOTf **3** is used as the substrate instead of PhBr **2**, the catalyst $Pd_2(dba)_3$/dppf performs not as well as before, and only 30% yield is achieved (Table 1, entry 14). Interestingly, this result can be significantly improved by switching the Pd(0) precursor to Pd(II) complexes. The use of $PdCl_2$(dppp) or in situ generated complex affords desired product in >95% yield (Table 1, entries 15−17). Both C−P coupling reactions with aryl bromides and triflates can be carried out successfully in gram scale catalyzed by $Pd_2(dba)_3$/dppf and $PdCl_2$(dppp), respectively.

Having optimized the reaction conditions, we examine the scope of this reaction using acylphosphines (Ar^2 = 4-MePh, Ph) as phosphination reagents. As shown in Scheme 2, various substituted aryl bromides react with acylphosphines and afford corresponding trivalent phosphines in good to excellent yields catalyzed by $Pd_2(dba)_3$/dppf. The results show that the reactivity of acylphosphines is robust to both electric and steric effects of substituted aryl groups. The hetero-aryl bromide can also react well, for example, 4-pyridyl bromide converts in a yield of 73% (Scheme 2, **13**). Varying the R group on phosphorus atom to *p*-Tol, cyclohexyl, and even 1-adamantyl, the corresponding acylphosphines react well with various aryl bromides (Scheme 2, **15**−**19**). The di-bromide substrate is also readily available with a double amount of catalyst and reagents (Scheme 2, **14**).

Switching the catalyst to $PdCl_2$(dppp), the substrate scope of this reaction is investigated with aryl triflates, which are more popularly used in the synthesis of backbone-diverse phosphine ligands. As shown in Scheme 3, the scope of the reaction reveals that the reaction accommodates a wide range of functional groups on aryl triflates. Notably, some sensitive groups, such as the protected amino group and coumarin, survive from the coupling condition, and successfully remain in the phosphine products (Scheme 3, **30**, **31**). With this method, a commercially available chiral monophosphine ligand **33** can be synthesized with complete retention of binaphthyl's chirality.

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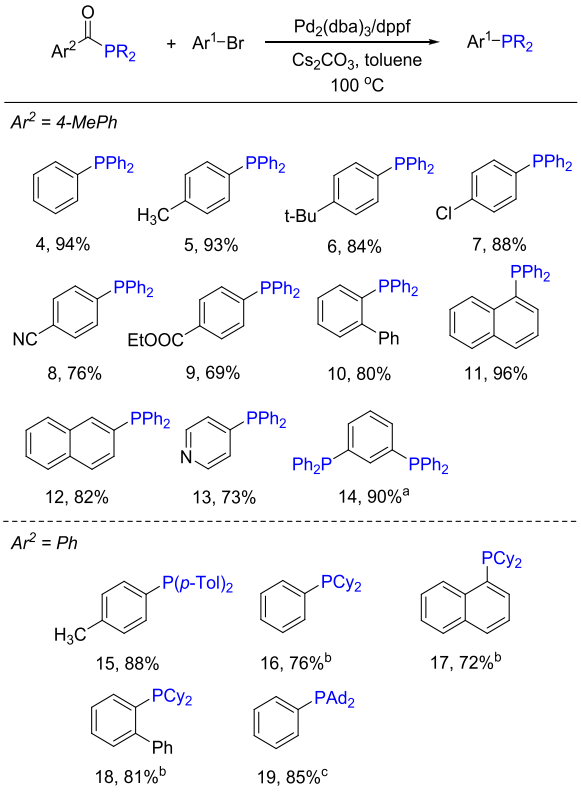
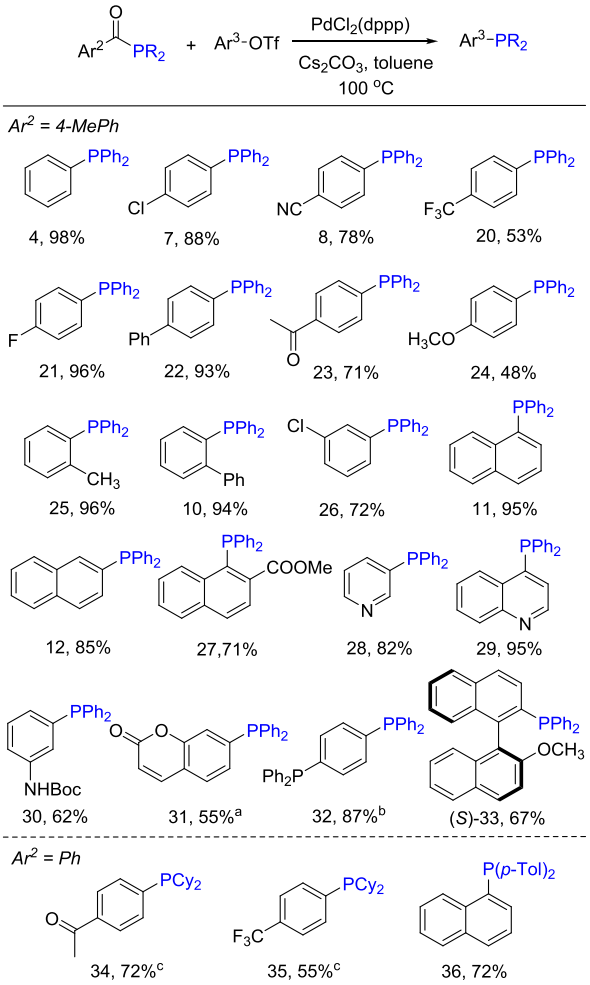
Scheme 2. Substrate Scope of Aryl Bromides[d]



[a]Acylphosphine (0.40 mmol), aryl dibromide (0.20 mmol), toluene (1.0 mL), Cs_2CO_3 (0.44 mmol), $Pd_2(dba)_3$ (5 mol %), and dppf (10 mol %) was used. [b]Under 120 °C, characterized by the phosphine oxide. [c]Cs_2CO_3 (0.30 mmol) was used, under 130 °C, characterized by the phosphine oxide. [d]Reaction conditions: acylphosphine (0.2 mmol), aryl bromide (0.21 mmol), toluene (0.5 mL), Cs_2CO_3 (0.22 mmol), $Pd_2(dba)_3$ (2.5 mol %), dppf (5 mol %), in N_2 under 100 °C for 12 h; isolated yield.

Scheme 3. Substrate Scope of Aryl Triflates[d]

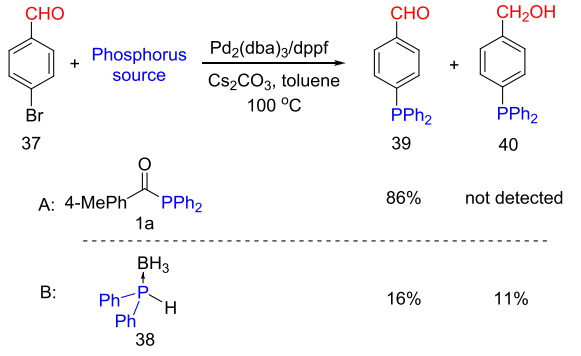


[a]Cs_2CO_3 (0.16 mmol) was used. [b]Acylphosphine (0.40 mmol), aryl ditriflate (0.20 mmol), toluene (1.0 mL), Cs_2CO_3 (0.44 mmol), and $PdCl_2(dppp)$ (10 mol %) was used. [c]Under 120 °C, characterized by the phosphine oxide. [d]Reaction conditions: acylphosphine (0.2 mmol), aryl triflate (0.21 mmol), toluene (0.5 mL), Cs_2CO_3 (0.22 mmol), $PdCl_2(dppp)$ (5 mol %), in N_2 under 100 °C for 12 h; isolated yield.

As we previously mentioned, using phosphine-borane complexes as the phosphorus source is an alternative way for phosphine synthesis. However, the borane BH_3 in the complexes tends to react with the electron-deficient unsaturated groups at the temperature that the coupling reactions occur.[10] Notably, an advantage of using acylphosphines is their good tolerance to the electrophilic functional groups. As shown in Scheme 4, under the optimized condition, the 4-bromobenzaldehyde **37** reacts with the acylphosphine **1a** and affords the aldehyde product **39** in a yield of 86%, with no detection of the reduced product **40**. However, changing acylphosphine **1a** into the phosphine-borane complex **38**, the reaction affords both the aldehyde and the alcohol product in yields of 16% and 11%, respectively.

A plausible mechanism of this reaction is proposed as shown in Figure 2. Pd(0) species **V** coordinates with the acylphosphine **I** and generates the complex **VI**. The complex **VI** undergoes oxidative addition with the electrophilic partner **II** or **III** to generate the intermediate **VII**. The consequent reductive elimination and de-acylation of **VII** release the desired product trivalent phosphine **IV** and regenerate Pd(0) species.

Scheme 4. FG Tolerance: Acylphosphine vs $HPPh_2{\cdot}BH_3$



CONCLUSIONS

In summary, we have developed a palladium-catalyzed C–P bond formation reaction of ArBr/ArOTf using acylphosphines as differential phosphination reagents. As trivalent phosphines, the acylphosphines usually show up as solids at room

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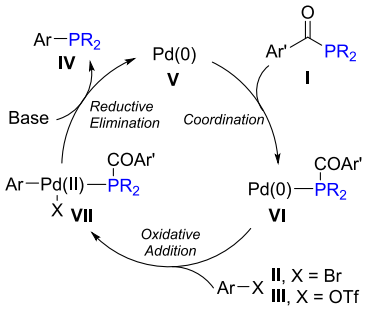

Figure 2. Plausible Mechanism.

temperature and are inert to air and moisture. As the phosphination reagents in reaction, they show practicable reactivity with ArBr and ArOTf and afford trivalent phosphines directly in good yields with a broad substrate scope and functional group tolerance. Considering our previous studies on acylphosphines' reactivity with aryl iodides and alkyl halides, this reaction further discloses their capability as a new phosphorus source for direct synthesis of trivalent phosphines. Other applications of acylphosphines in phosphine synthesis will be reported in due course.

EXPERIMENTAL SECTION

General Information. Unless otherwise specified, all reactions were performed under a dry N_2 atmosphere. Anhydrous solvents were distilled prior to use. Toluene and tetrahydrofuran were distilled from sodium using benzophenone as the indicator. Dichloromethane was distilled from CaH_2. Sensitive reagents and solvents were transferred under nitrogen in a glove-box using standard techniques. Reaction temperatures are reported as the temperatures of the bath surrounding the vessels. An oil bath was used for the reactions in Schlenk flasks, and a heating block was used for the reactions in sealed vials. Unless otherwise noted, all commercial materials were purchased from Energy Chemical and used without further purification. Acylphosphines **1** were prepared according to previously described procedures.[11] Proton nuclear magnetic resonance (^{1}H NMR), carbon nuclear magnetic resonance (^{13}C NMR), phosphorus nuclear magnetic resonance (^{31}P NMR), and fluorine nuclear magnetic resonance (^{19}F NMR) were recorded on a Bruker Avance III 400 at 400, 101, 162, and 376 MHz, respectively. Spectra were recorded in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ = 0.00 ppm) and are referenced to residual solvent ($CDCl_3$, δ = 7.26 ppm (^{1}H) and 77.16 ppm (^{13}C)). In the quantitative ^{31}P NMR spectra, chemical shifts were recorded using triphenyl phosphite as the internal standard. Coupling constants (J) are reported in hertz (Hz) and the resonance multiplicity abbreviations used are: s, singlet; d, doublet; t, triplet; q, quartet; dt, doublet of triplets; td, triplet of doublets; dd, doublet of doublets; ddd, doublet of doublet of doublets; m, multiplet. The high-resolution mass spectra were obtained under ESI ionization using an LC/MSD TOF mass spectrometer. Infrared (IR) spectra were obtained with a FT-IR series spectrometer as thin films on potassium bromide plates. Thin-layer chromatography (TLC) was performed on GF254 silica gel coated plates and were visualized using one or more of the following methods: UV light (254 nm) and staining with alkaline potassium permanganate ($KMnO_4$). Flash chromatography was performed using glass columns and carried out on SiO_2 (silica gel 200−300 mesh).

General Procedure A: Preparation of Acylphosphines. Containing a solution of secondary phosphine (5.25 mol) in 10 mL of tetrahydrofuran, an oven-dried Schlenk tube was charged with triethylamine (0.64 g, 6.3 mmol) under a N_2 atmosphere, followed by addition of acyl chloride (5.5 mmol). After stirring at room temperature for about 6 h, the reaction was complete (monitored by TLC). The mixture was filtrated through celite, and the volatiles were removed using a rotary evaporator. The residue was recrystallized from 10 mL of methanol to afford the acylphosphine **1**.

*p-Methylbenzoyldiphenylphosphine (**1a**).* According to the general procedure **A**, reaction with diphenylphosphine (0.98 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol), and 4-methylbenzoyl chloride (0.85 g, 5.5 mmol) afforded 1.24 g (78%) of the product as a yellow amorphous solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90−7.87 (m, 2H), 7.42−7.40 (m, 5H), 7.38−7.34 (m, 5H), 7.14 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H). ^{31}P{^{1}H} ($CDCl_3$, 162 MHz): δ 12.64. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{20}H_{18}OP^+$ 305.1090; Found 305.1088. IR (film): 1641, 1600, 1436, 1180, 1143, 1075, 901, 696 cm^{-1}.

*(Di-p-Tolylphosphanyl)(phenyl)methanone (**1b**).* According to the general procedure **A**, reaction with di-*p*-tolylphosphane (1.12 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol), and benzoyl chloride (0.77 g, 5.5 mmol) afforded 1.29 g (77%) of the product as a pale yellow amorphous solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.96 (d, J = 8.3 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.36−7.25 (m, 6H), 7.15 (d, J = 7.5 Hz, 4H), 2.32 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 213.5 (d, J = 37.1 Hz), 139.6, 139.4 (d, J = 34.3 Hz), 134.9 (d, J = 19.0 Hz), 133.0, 129.6 (d, J = 8.1 Hz), 129.4 (d, J = 4.0 Hz), 128.5, 128.3 (d, J = 9.1 Hz), 21.4. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 11.84. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{21}H_{20}OP^+$ 319.1246; Found 319.1240. IR (film): 1645, 1600, 1447, 1205, 1173, 1116, 806, 710, 691, 531 cm^{-1}.

*(Dicyclohexylphosphanyl)(phenyl)methanone (**1c**).* According to the general procedure **A**, reaction with dicyclohexylphosphane (1.04 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol), and benzoyl chloride (0.77 g, 5.5 mmol) afforded 1.08 g (68%) of the product as a yellow amorphous solid. This product contained 10% decomposed product after handling in air. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01 (d, J = 8.0 Hz, 2H), 7.58−7.43 (m, 3H), 2.04−1.99 (m, 2H), 1.77−1.62 (m, 10H), 1.31−1.10 (m, 10H); ^{31}P{^{1}H} ($CDCl_3$, 162 MHz): δ 18.93. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{19}H_{28}OP^+$ 303.1872; Found 303.1865. IR (film): 2925, 2850, 1637, 1578, 1446, 1208, 1170, 902, 772, 692 cm^{-1}.

*(Di(adamantan-1-yl)phosphanyl)(phenyl)methanone (**1d**).* According to the general procedure **A**, reaction with di(adamantan-1-yl)phosphane (1.59 g, 5.25 mmol), triethylamine (0.64 g, 6.3 mmol), and benzoyl chloride (0.77 g, 5.5 mmol) afforded 1.90 g (89%) of the product as an orange amorphous solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15−8.12 (m, 2H), 7.56−7.52 (m, 1H), 7.44 (t, J = 7.6 Hz, 2H), 2.08−2.04 (m, 6H), 1.96−1.90 (m, 12H), 1.69 (s, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 218.2 (d, J = 49.4 Hz), 144.1 (d, J = 34.6 Hz), 133.2 (d, J = 1.6 Hz), 128.8 (d, J = 12.7 Hz), 128.4 (d, J = 1.7 Hz), 41.5 (d, J = 9.8 Hz), 38.4 (d, J = 22.7 Hz), 36.8, 28.8 (d, J = 8.2 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 39.01. HRMS (ESI/Q-TOF) m/z: [M + H]$^+$ Calcd for $C_{27}H_{36}OP^+$ 407.2498; Found 407.2499. IR (film): 2900, 2846, 1633, 1445, 1197, 1168, 894, 766, 688 cm^{-1}.

General Procedure B: Phosphination with Aryl Bromides. Under a N_2 atmosphere, acylphosphine (0.2 mmol), aryl bromide (0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) were mixed in a sealed vial and stirred at 100 °C for 12 h using a heating block. After the reaction was allowed to cool down to room temperature, the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel to afford pure desired product.

General Procedure C: Phosphination with Aryl Trifluoromethanesulfonates. Under a N_2 atmosphere, acylphosphine (0.2 mmol), aryl triflate (0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) were mixed in a sealed vial and stirred at 100 °C for 12 h using a heating block. After the reaction was complete and cooled to room temperature, the solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel to afford pure desired product.

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Large-Scale Preparation of Triphenylphosphane ***4***. According to the general procedure **B**, under a N_2 atmosphere, *p*-methylbenzoyldiphenylphosphine **1a** (1.22 g, 4.0 mmol, 1.0 equiv), bromobenzene (0.66 g, 4.2 mmol, 1.05 equiv), toluene (10 mL), Cs_2CO_3 (1.43 g, 4.4 mmol, 1.1 equiv), $Pd_2(dba)_3$ (92 mg, 0.1 mmol, 2.5 mol %), and dppf (111 mg, 0.2 mmol, 5 mol %) were mixed in a sealed Schlenk flask and stirred at 100 °C for 24 h using an oil bath. After the reaction was allowed to cool down to room temperature, the mixture was transferred with 30 mL of dichloromethane, and the insoluble composition is filtered. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel (eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc), and **4** (0.98 g) was afforded in a yield of 93% as a white amorphous solid.

According to the general procedure **C**, under a N_2 atmosphere, *p*-methylbenzoyldiphenylphosphine **1a** (1.22 g, 4.0 mmol, 1.0 equiv), phenyl trifluoromethanesulfonate (0.95 g, 4.2 mmol, 1.05 equiv), toluene (10 mL), Cs_2CO_3 (1.43 g, 4.4 mmol, 1.1 equiv), and $PdCl_2$(dppp) (118 mg, 0.2 mmol, 5 mol %) were mixed in a sealed Schlenk flask and stirred at 100 °C for 24 h using an oil bath. After the reaction was allowed to cool down to room temperature, the mixture was transferred with 30 mL of dichloromethane, and the insoluble composition is filtered. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel (eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc) to afford **4** (0.92 g) was afforded in a yield of 88% as a white amorphous solid.

*Triphenylphosphane (****4****).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), bromobenzene (33 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **4** (49.3 mg) in a yield of 94% as a white amorphous solid. According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), phenyl trifluoromethanesulfonate (47.5 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **4** (51.4 mg) in a yield of 98% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.25 (m, 15H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −5.37. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{16}P^+$ 263; Found 263. IR (film): 3067, 1474, 1431, 1087, 1068, 1026, 741, 694, 510, 494 cm^{-1}.

*Diphenyl(p-tolyl)phosphane (****5****).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (2.5 g, 0.20 mmol, 1.0 equiv), 1-bromo-4-methylbenzene (35.9 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **5** (51.4 mg) in a yield of 93% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34−7.27 (m, 10H), 7.24−7.14 (m, 4H), 2.35 (s, 3H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −6.22. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}P^+$ 277; Found 277. IR (film): 3051, 2918, 1433, 1265, 1090, 1026, 807, 742, 696, 511 cm^{-1}.

*(4-tert-Butyl)phenyl)diphenylphosphane (****6****).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 1-bromo-4-(*tert*-butyl)-benzene (44.8 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **6** (53.5 mg) in a yield of 84% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37−7.22 (m, 14H), 2.35 (s, 9H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −6.48. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{24}P^+$ 319; Found 319. IR (film): 3070, 2962, 2903, 1493, 1433, 1084, 820, 744, 696, 560, 496 cm^{-1}.

*(4-Chlorophenyl)diphenylphosphane (****7****).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 1-bromo-4-chlorobenzene (40.2 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **7** (52.2 mg) in a yield of 88% as a white amorphous solid. According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 4-chlorophenyl trifluoromethanesulfonate (54.7 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **7** (52.2 mg) in a yield of 88% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36−7.20 (m, 14H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −6.41. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}ClP^+$ 297; Found 297. IR (film): 3069, 3053, 1584, 1478, 1433, 1384, 1070, 1013, 817, 738, 695, 506 cm^{-1}.

*4-(Diphenylphosphanyl)benzonitrile (****8****).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzonitrile (38.2 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **8** (43.7 mg) in a yield of 76% as a white amorphous solid. According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 4-cyanophenyl trifluoromethanesulfonate (52.7 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **8** (44.8 mg) in a yield of 78% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 20/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, J = 8 Hz, 2H), 7.58−7.25 (m, 12H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −4.27. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}NP^+$ 288; Found 288. IR (film): 3048, 2356, 2221, 1594, 1488, 1433, 1385, 1087, 822, 693 cm^{-1}.

*Ethyl 4-(Diphenylphosphanyl)benzoate (****9****).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), ethyl 4-bromobenzoate (48.1 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **9** (46.1 mg) in a yield of 69% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (dd, J = 8.0, 4.0 Hz, 2H), 7.37−7.29 (m, 12H), 4.37 (q, 2H), 1.37 (t, 3H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ: -5.06. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{20}O_2P^+$ 335; Found 335. IR (film): 3052, 2980, 1717, 1593, 1435, 1276, 1109, 1020, 745, 696 cm^{-1}.

*[1,1′-Biphenyl]-2-yldiphenylphosphane (****10****).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 2-bromo-1,1′-biphenyl (49 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **10** (54.1 mg) in a yield of 80% as a white amorphous solid. According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), [1,1′-biphenyl]-2-yl trifluoromethanesulfonate (63.5 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **10** (63.6 mg) in a yield of 94% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38−7.17 (m, 18H), 7.07−7.05 (m,1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −13.43. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}P^+$ 339; Found 339. IR (film): 3051, 1582, 1461, 1433, 1088, 1003, 914, 746, 698, 496 cm^{-1}.

*Naphthalen-1-yldiphenylphosphane (****11****).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 1-bromonaphthalene (43.5 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **11** (60.0 mg) in a

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yield of 96% as a white amorphous solid. According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), naphthalen-1-yl trifluoromethanesulfonate (58 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **11** (59.3 mg) in a yield of 95% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.41 (dd, J = 8.0, 4.0 Hz, 1H), 7.85 (t, J = 8.0 Hz, 2H), 7.50−7.41 (m, 2H), 7.37−7.28 (m, 11H), 7.02−6.98 (m, 1H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −14.18. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}P^+$ 313; Found 313. IR (film): 3051, 1433, 1265, 796, 774, 743, 696, 501, 446 cm^{-1}.

*Naphthalen-2-yldiphenylphosphane (**12**).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 2-bromonaphthalene (43.5 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **12** (51.2 mg) in a yield of 82% as a white amorphous solid. According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), naphthalen-2-yl trifluoromethanesulfonate (58 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **12** (53.1 mg) in a yield of 85% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83−7.78 (m, 3H), 7.74−7.72 (m, 1H), 7.51−7.44 (m, 2H), 7.40−7.31 (m, 11H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −4.84. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}P^+$ 313; Found 313. IR (film): 3051, 1584, 1478, 1433, 1269, 1091, 1025, 817, 741, 695, 638, 475 cm^{-1}.

*4-(Diphenylphosphanyl)pyridine (**13**).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 4-bromopyridine hydrochloride (62.9 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **13** (38.4 mg) in a yield of 73% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 4/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52−8.50 (m, 2H), 7.41−7.33 (m,10H), 7.12−7.09 (m, 2H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −6.95. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}NP^+$ 264; Found 264. IR (film): 3051, 2359, 1571, 1430, 1405, 1312, 1091, 745, 697, 495 cm^{-1}.

*1,3-Bis(diphenylphosphanyl)benzene (**14**).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (121.7 mg, 0.40 mmol, 2.0 equiv), 1,3-dibromobenzene (47.2 mg, 0.2 mmol, 1.0 equiv), toluene (1.0 mL), Cs_2CO_3 (143.4 mg, 0.44 mmol, 2.2 equiv), $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol, 5 mol %), and dppf (11.1 mg, 0.02 mmol, 10 mol %) afforded **14** (80.4 mg) in a yield of 90% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33−7.18 (m, 24H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −5.33. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}P_2^+$ 447; Found 447. IR (film): 3058, 1715, 1435, 1157, 742, 695, 544, 526 cm^{-1}.

*Tri-p-tolylphosphane (**15**).* According to the general procedure **B**, reaction with (di-*p*-tolylphosphanyl)(phenyl)methanone **1b** (63.7 mg, 0.20 mmol, 1.0 equiv), 1-bromo-4-methylbenzene (35.9 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **15** (53.6 mg) in a yield of 88% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25−7.17 (m, 6H), 7.14−7.12 (m, 6H), 2.34 (s, 9H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −7.87. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}P^+$ 305; Found 305. IR (film): 3054, 1722, 1430, 1134, 751, 685, 543, 522 cm^{-1}.

*Diphenyl(4-(trifluoromethyl)phenyl)phosphine (**20**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 4-(trifluoromethyl)-phenyl trifluoromethanesulfonate (61.8 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **20** (35.0 mg) in a yield of 53% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, J = 8.0 Hz, 2H), 7.39−7.29 (m, 12H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −5.35. ^{19}F NMR ($CDCl_3$, 376 MHz): δ −62.75. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}F_3P^+$ 331; Found 331. IR (film): 3067, 1606, 1479, 1434, 1395, 1324, 1166, 1126, 1106, 1016, 832, 743, 697, 504 cm^{-1}.

*(4-Fluorophenyl)diphenylphosphane (**21**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 4-fluorophenyl trifluoromethanesulfonate (51.3 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **21** (53.8 mg) in a yield of 96% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.25 (m, 12H), 7.06−7.01 (m, 2H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −6.66 (d, J = 4.1 Hz). MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}FP^+$ 281; Found 281. IR (film): 3067, 1588, 1493, 1433, 1231, 1159, 828, 725, 696, 522 cm^{-1}.

*[1,1′-Biphenyl]-4-yldiphenylphosphane (**22**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), [1,1′-biphenyl]-4-yl trifluoromethanesulfonate (63.5 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **22** (62.9 mg) in a yield of 93% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (t, J = 8.0 Hz, 4H), 7.45−7.35 (m, 15H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −6.05. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}P^+$ 339; Found 339. IR (film): 3052, 1479, 1433, 1385, 1092, 1006, 832, 761, 743, 695, 502 cm^{-1}.

*1-(4-(Diphenylphosphanyl)phenyl)ethan-1-one (**23**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 4-acetylphenyl trifluoromethanesulfonate (53.6 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **23** (43.2 mg) in a yield of 71% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (dd, J = 8.0, 4.0 Hz ,2H), 7.38−7.26 (m,12H), 2.59 (s, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −5.01. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{18}OP^+$ 305; Found 305. IR (film): 3052, 1684, 1592, 1478, 1433, 1262, 824, 743, 696, 495 cm^{-1}.

*(4-Methoxyphenyl)diphenylphosphane (**24**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 4-methoxyphenyl trifluoromethanesulfonate (53.8 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **24** (28.1 mg) in a yield of 48% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33−7.24 (m, 12H), 6.89 (d, J = 8.0 Hz, 2H), 3.81 (s, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −7.00. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}OP^+$ 293; Found 293. IR (film): 3051, 3000, 1594, 1567, 1497, 1478, 1433, 1247, 1177, 1094, 1028, 826, 743, 696 cm^{-1}.

*Diphenyl(o-tolyl)phosphane (**25**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), *o*-tolyl trifluoromethanesulfonate (50.4 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **25** (53.1 mg) in a yield of 96% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35−7.19 (m, 12H), 7.08 (t, J = 8.0 Hz, 1H), 6.78−6.75 (m,1H), 2.39 (s, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −13.30. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}P^+$ 277; Found 277. IR (film): 3052, 1475, 1433, 1091, 1026, 743, 696, 503, 465 cm^{-1}.

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*(3-Chlorophenyl)diphenylphosphane (**26**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 3-chlorophenyl trifluoromethanesulfonate (54.7 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **26** (42.7 mg) in a yield of 72% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36−7.23 (m, 13H), 7.19−7.15 (m, 1H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −4.95. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{15}ClP^+$ 297; Found 297. IR (film): 3053, 1577, 1559, 1477, 1463, 1433, 1118, 742, 695, 502 cm^{-1}.

*Methyl 1-(Diphenylphosphanyl)-2-naphthoate (**27**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), methyl 1-(((trifluoromethyl)sulfonyl)oxy)-2-naphthoate (70.2 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **27** (52.6 mg) in a yield of 71% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 20/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18 (dd, J = 8.0, 4.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.60 (dd, J = 8.0, 4.0 Hz, 1H), 7.45−7.39 (m, 5H), 7.30−7.23 (m, 7H), 3.61 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 170.1 (d, J = 3.4 Hz), 140.5 (d, J = 26.3 Hz), 135.7 (d, J = 12.6 Hz), 134.9 (d, J = 6.8 Hz), 134.4 (d, J = 2.0 Hz), 132.5 (d, J = 18.8 Hz), 131.9 (d, J = 25.6 Hz), 131.3 (d, J = 1.3 Hz), 128.9, 128.6 (d, J = 14.1 Hz), 128.4 (d, J = 6.1 Hz), 128.1, 126.9, 126.6, 124.7 (d, J = 7.4 Hz), 52.2. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −9.50. HRMS (ESI-QTOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}O_2P^+$ 371.1195; Found 371.1199. IR (film): 3052, 1684, 1592, 1478, 1433, 1262, 824, 743, 696, 495 cm^{-1}.

*3-(Diphenylphosphanyl)pyridine (**28**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), pyridin-3-yl trifluoromethanesulfonate (47.7 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **28** (43.2 mg) in a yield of 82% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 4/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (d, J = 4.0 Hz, 1H), 8.52 (s, 1H), 7.58−7.54 (m, 1H), 7.37−7.24 (m, 11H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −11.76. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{15}NP^+$ 264; Found 264. IR (film): 3069, 1557, 1478, 1433, 1399, 1089, 1021, 743, 698, 500 cm^{-1}.

*4-(Diphenylphosphanyl)quinoline (**29**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), quinolin-4-yl trifluoromethanesulfonate (58.2 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **29** (59.5 mg) in a yield of 95% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 4/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.86 (d, J = 3.3 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.47−7.36 (m, 2H), 7.30−7.29 (m, 10H), 7.12 (dd, J = 6.4, 3.7 Hz, 1H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −14.94. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}NP^+$ 314.1093; Found 314.1100. IR (film): 1490, 1432, 828, 794, 743, 696, 553, 498, 457, 424 cm^{-1}.

*tert-Butyl (3-(Diphenylphosphanyl)phenyl)carbamate (**30**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 3-((*tert*-butoxycarbonyl)amino)phenyl trifluoromethanesulfonate (71.7 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **30** (46.8 mg) in a yield of 62% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 10/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65−7.63 (m, 1H), 7.39−7.27 (m, 11H), 7.00−6.93 (m, 2H), 6.37 (br s, 1H), 1.48 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 152.6, 138.6 (d, J = 8.3 Hz), 138.1 (d, J = 11.5 Hz), 137.0 (d, J = 11.0 Hz), 133.8 (d, J = 19.6 Hz), 129.3 (d, J = 7.2 Hz), 128.8, 128.5 (d, J = 6.9 Hz), 128.3 (d, J = 18.5 Hz), 123.4 (br d, J = 21.5 Hz), 119.1, 80.6, 28.3. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −5.09. HRMS (ESI-QTOF) m/z: $([M + H]^+)$ Calcd for $C_{23}H_{25}NO_2P^+$ 378.1617; Found 378.1625. IR (film): 3326, 2977, 1728, 1704, 1593, 1454, 1159, 1057, 832, 743, 697, 504 cm^{-1}.

*7-(Diphenylphosphanyl)-2H-chromen-2-one (**31**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 2-oxo-2*H*-chromen-7-yl trifluoromethanesulfonate (61.8 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (52.1 mg, 0.16 mmol, 0.8 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **31** (36.3 mg) in a yield of 55% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 4/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, J = 9.5 Hz, 1H), 7.45−7.31 (m, 11H), 7.26−7.20 (m, 1H), 7.11 (d, J = 5.8 Hz, 1H), 6.41 (d, J = 9.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 101 MHz): δ 160.5, 153.9 (d, J = 6.2 Hz), 144.1 (d, J = 16.4 Hz), 143.0, 135.6 (d, J = 10.6 Hz), 134.0 (d, J = 20.2 Hz), 129.5, 129.1 (d, J = 22.8 Hz), 128.9 (d, J = 7.4 Hz), 127.4 (d, J = 8.1 Hz), 121.0 (d, J = 14.8 Hz), 118.6, 117.0. ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −4.18. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{16}O_2P^+$ 331.0882; Found 331.0886. IR (film): 1736, 1604, 1434, 1389, 1173, 1146, 1100, 843, 747, 697 cm^{-1}.

*1,4-Bis(diphenylphosphanyl)benzene (**32**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (121.7 mg, 0.40 mmol, 2.0 equiv), 1,4-phenylene bis(trifluoromethanesulfonate) (74.8 mg, 0.2 mmol, 1.0 equiv), toluene (1.0 mL), Cs_2CO_3 (143.4 mg, 0.44 mmol, 2.2 equiv), and $PdCl_2$(dppp) (11.8 mg, 0.02 mmol, 10 mol %) afforded **32** (77.7 mg) in a yield of 87% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.29 (m, 20H), 7.24−7.22 (m, 4H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −5.69. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{25}P_2^+$ 447.1426; Found 447.1427. IR (film): 3051, 1476, 1433, 1090, 1021, 742, 694, 507 cm^{-1}.

*(S)-(2′-Methoxy-[1,1′-binaphthalen]-2-yl)diphenylphosphane ((S)-**33**).* According to the general procedure **C**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), (*S*)-2′-methoxy-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (90.8 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded (*S*)-**33** (62.8 mg) in a yield of 67% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 20/1 PE/EtOAc. $[\alpha]_D^{20}$ −93.9° ($CHCl_3$, *c* 0.27) (literature rotation for (*S*)-**33** $[\alpha]_D^{20}$ −94.5° ($CHCl_3$, *c* 0.27)[12]). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 9.0 Hz, 1H), 7.91−7.81 (m, 3H), 7.48−7.42 (m, 1H), 7.39 (dd, J = 8.5, 2.8 Hz, 1H), 7.32−7.03 (m, 15H), 6.93 (d, J = 8.4 Hz, 1H), 3.35 (s, 3H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −13.71. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{26}OP^+$ 469; Found 469. IR (film): 2927, 1622, 1593, 1434, 1265, 1252, 1038, 1060, 740, 694 cm^{-1}.

*Naphthalen-1-yldi-p-tolylphosphane (**36**).* According to the general procedure **C**, reaction with (di-*p*-tolylphosphanyl)(phenyl)-methanone **1b** (63.7 mg, 0.20 mmol, 1.0 equiv), naphthalen-1-yl trifluoromethanesulfonate (58.0 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2$(dppp) (5.90 mg, 0.01 mmol, 5 mol %) afforded **36** (49.0 mg) in a yield of 72% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 30/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40−8.36 (m, 1H), 7.835 (dd, J = 8.0, 12.0 Hz, 2H), 7.48−7.40 (m, 2H), 7.36−7.32 (m, 1H), 7.21−7.16 (m, 8H), 7.14−6.98 (m, 1H), 2.34 (s, 6H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ −15.90. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}P^+$ 341; Found 341. IR (film): 3079, 1567, 1473, 1432, 1393, 1080, 1026, 745, 698, 502 cm^{-1}.

*4-(Diphenylphosphanyl)benzaldehyde (**39**).* According to the general procedure **B**, reaction with *p*-methylbenzoyldiphenylphosphine **1a** (61 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde (38.9 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **39** (49.9 mg) in a yield of 86% as a white amorphous solid. According to the general procedure **B**, reaction with (diphenylphosphine)trihydroboron **38**

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(40.0 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde (38.9 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **39** (9.3 mg) in a yield of 16% as a white amorphous solid. Eluent for silica-gel column chromatography: 100/1 to 20/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.00 (s, 1H), 7.80 (dd, J = 8.2, 1.3 Hz, 2H), 7.44−7.30 (m, 12H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −4.33. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{16}OP^+$ 291; Found 291. IR (film): 3054, 1704, 1593, 1436, 1205, 1171, 1118, 748, 727, 694 cm^{-1}.

*(4-(Diphenylphosphanyl)Phenyl)Methanol (**40**).* According to the general procedure **B**, reaction with (diphenylphosphine)-trihydroboron **38** (40.0 mg, 0.20 mmol, 1.0 equiv), 4-bromobenzaldehyde (38.9 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **40** (6.4 mg) in a yield of 11% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 10/1 PE/EtOAc. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34−7.29 (m, 14H), 4.69 (s, 2H), 1.70 (br s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 141.5, 137.1 (d, J = 10.7 Hz), 136.6 (d, J = 10.8 Hz), 134.0 (d, J = 19.7 Hz), 133.7 (d, J = 19.5 Hz), 128.8, 128.5 (d, J = 6.9 Hz), 127.1 (d, J = 7.1 Hz), 65.0. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ −5.92. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}OP^+$ 293.1090; Found 293.1100. IR (film): 3378, 1435, 1171, 1117, 1091, 1051, 1020, 746, 725, 697, 540 cm^{-1}.

General Procedure D: Phosphination with Aryl Bromides Characterized by the Phosphine Oxide. For the consideration of stability, the desired product trivalent phosphine was separated and characterized by its corresponding phosphine oxide. Under a N_2 atmosphere, acylphosphine (0.2 mmol), aryl bromide (0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) were mixed in a sealed vial and stirred at 100 °C for 12 h using a heating block. After the reaction was allowed to cool down to room temperature, the solvent was removed under vacuum and methanol (1 mL) and H_2O_2 (30 wt % in H_2O, 0.2 mL) were added. The mixture was stirred at r.t. for 12 h, and then the reaction mixture was dried under vacuum. The residue was purified by flash chromatography on silica gel to afford pure desired product.

General Procedure E: Phosphination with Aryl Trifluoromethanesulfonates Characterized by the Phosphine Oxide. For the consideration of stability, the desired product trivalent phosphine was separated and characterized by its corresponding phosphine oxide. Under a N_2 atmosphere, acylphosphine (0.2 mmol), aryl triflate (0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2(dppp)$ (5.90 mg, 0.01 mmol, 5 mol %) were mixed in a sealed vial and stirred at 100 °C for 12 h using a heating block. After the reaction was allowed to cool down to room temperature, the solvent was removed under vacuum and methanol (1 mL) and H_2O_2 (30 wt % in H_2O, 0.2 mL) were added. The mixture was stirred at r.t. for 12 h, and then the reaction mixture was dried under vacuum. The residue was purified by flash chromatography on silica gel to afford the pure desired product.

*Dicyclohexyl(phenyl)phosphine Oxide (**16-Oxide Product**).* According to the general procedure **D**, reaction at 120 °C with (dicyclohexylphosphanyl)(phenyl)methanone **1c** (60.5 mg, 0.20 mmol, 1.0 equiv), bromobenzene (33.0 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **16-oxide product** (44.1 mg) in a yield of 76% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 30/1 DCM/MeOH. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69−7.64 (m, 2H), 7.54−7.45 (m, 3H), 2.03−2.00 (m, 4H), 1.84−1.60 (m, 8H), 1.38−1.09 (m, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 45.01. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{28}OP^+$ 291; Found 291. IR (film): 2932, 2855, 1514, 1497, 1145, 928, 882, 835, 738 cm^{-1}.

*Dicyclohexyl(naphthalen-1-yl)phosphine Oxide (**17-Oxide Product**).* According to the general procedure **D**, reaction at 120 °C with (dicyclohexylphosphanyl)(phenyl)methanone **1c** (60.5 mg, 0.20 mmol, 1.0 equiv), 1-bromonaphthalene (43.5 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **17-oxide product** (49.0 mg) in a yield of 72% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 30/1 DCM/MeOH. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.99 (s, 1H), 7.98 (d, J = 12.0 Hz, 1H), 7.89 (d, J = 4.0 Hz, 1H), 7.79−7.72 (m, 1H), 7.59−7.50 (m, 3H), 2.28−2.15 (m, 4H), 1.85−1.82 (m, 2H), 1.71−1.58 (m, 6H), 1.50−1.07 (m, 10H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 49.95. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{30}OP^+$ 341; Found 341. IR (film): 2938, 2852, 1504, 1447, 1155, 917, 889, 805, 776, 739, 540 cm^{-1}.

*[1,1′-Biphenyl]-2-yldicyclohexylphosphine Oxide (**18-Oxide Product**).* According to the general procedure **D**, reaction at 120 °C with (dicyclohexylphosphanyl)(phenyl)methanone **1c** (60.5 mg, 0.20 mmol, 1.0 equiv), 2-bromo-1,1′-biphenyl (49.0 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **18-oxide product** (59.4 mg) in a yield of 81% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 30/1 DCM/MeOH. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.14−8.09 (m, 1H), 7.50−7.42 (m, 5H), 7.23−7.20 (m, 3H), 1.84−1.53 (m, 10H), 1.40−1.28 (m, 6H), 1.21−0.98 (m, 6H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 48.21. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{32}OP^+$ 367; Found 367. IR (film): 2938, 2856, 1504, 1487, 1145, 918, 889, 825, 776, 732 cm^{-1}.

*Di(adamantan-1-yl)(phenyl)phosphine Oxide (**19-Oxide Product**).* According to the general procedure **D**, reaction at 130 °C with (di(adamantan-1-yl)phosphanyl)(phenyl)methanone **1d** (81.3 mg, 0.20 mmol, 1.0 equiv), bromobenzene (33.0 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (97.7 mg, 0.3 mmol, 1.5 equiv), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol %), and dppf (5.6 mg, 0.01 mmol, 5 mol %) afforded **19-oxide product** (67.1 mg) in a yield of 85% as a light yellow amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 30/1 DCM/MeOH. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05−8.01 (m, 1H), 7.61−7.40 (m, 4H), 2.11−1.96 (m, 18H), 1.72−1.67 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 101 MHz): δ 134.8, 130.7 (d, J = 2.6 Hz), 130.5 (d, J = 9.9 Hz), 130.0 (d, J = 77.4 Hz), 128.6 (d, J = 9.2 Hz), 126.7 (d, J = 10.7 Hz), 39.9 (d, J = 60.7 Hz), 37.1, 36.6, 27.9 (d, J = 9.0 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 42.93. HRMS (ESI/Q-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{36}OP^+$ 395.2498; Found 395.2507. IR (film): 2962, 2923, 1844, 1487, 1132, 933, 843, 835, 718 cm^{-1}.

*1-(4-(Dicyclohexylphosphoryl)phenyl)ethan-1-one (**34-Oxide Product**).* According to the general procedure **E**, reaction at 120 °C with (dicyclohexylphosphanyl)(phenyl)methanone **1c** (60.5 mg, 0.20 mmol, 1.0 equiv), 4-acetylphenyl trifluoromethanesulfonate (56.3 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2(dppp)$ (5.90 mg, 0.01 mmol, 5 mol %) afforded **34-oxide product** (47.9 mg) in a yield of 72% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 30/1 DCM/MeOH. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.06−8.03 (m, 2H), 7.81−7.77 (m, 2H), 2.65 (s, 3H), 2.07−2.05 (m, 4H), 1.85−1.59 (m, 8H), 1.35−1.09 (m, 10H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 197.7, 139.1 (d, J = 2.6 Hz), 135.8 (d, J = 81.1 Hz), 131.9 (d, J = 7.8 Hz), 127.8 (d, J = 10.4 Hz), 35.2 (d, J = 67.1 Hz), 26.8, 26.4 (d, J = 12.8 Hz), 26.3 (d, J = 12.3 Hz), 25.8 (d, J = 1.0 Hz), 25.5 (d, J = 2.6 Hz), 24.6 (d, J = 3.3 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 44.92. HRMS (ESI-QTOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{30}O_2P^+$ 333.1978; Found 333.1985. IR (film): 3252, 1784, 1583, 1468, 1444, 1269, 821, 744, 693, 490 cm^{-1}.

*Dicyclohexyl(4-(trifluoromethyl)phenyl)phosphine Oxide (**35-Oxide Product**).* According to the general procedure **E**, reaction at 120 °C with (dicyclohexylphosphanyl)(phenyl)methanone **1c** (60.5 mg, 0.20 mmol, 1.0 equiv), 4-(trifluoromethyl)phenyl trifluoromethanesulfonate (61.8 mg, 0.21 mmol, 1.05 equiv), toluene (0.5 mL), Cs_2CO_3 (71.7 mg, 0.22 mmol, 1.1 equiv), and $PdCl_2(dppp)$ (5.90 mg, 0.01 mmol, 5 mol %) afforded **35-oxide product** (39.4 mg) in a yield of 55% as a white amorphous solid. Eluent for silica-gel column chromatography: 50/1 to 30/1 DCM/MeOH. ^{1}H NMR ($CDCl_3$, 400

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MHz): δ 7.83−7.79 (m, 2H), 7.74−7.73 (m, 2H), 2.07−2.02 (m, 4H), 1.86−1.58 (m, 8H), 1.35−1.13 (m, 10H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz): δ 44.59. MS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{27}F_3OP^+$ 359; Found 359. IR (film): 2927, 2853, 1446, 1397, 1325, 1175, 1132, 1062, 1011, 844, 699, 605, 563, 537 cm^{-1}.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00937.

Experimental procedures and characterization data for all new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Hong Zhu − *State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China;* orcid.org/0000-0003-4074-5229; Email: zhuho128@126.com

Zhiqian Wang − *State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China;* orcid.org/0000-0001-9831-649X; Email: wangzhq@mail.buct.edu.cn

Authors

Xingyu Chen − *State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China*

Hongyu Wu − *State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China*

Rongrong Yu − *State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.1c00937

Notes

The authors declare no competing financial interest.

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