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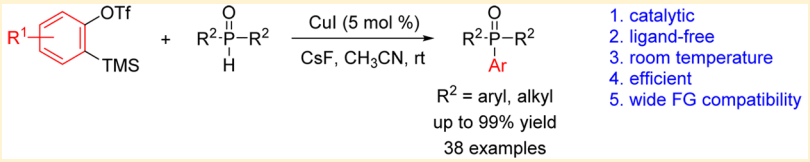
Copper-Catalyzed Addition of H−P(O) Bonds to Arynes

Qian Chen,* Xinxing Yan, Chunxiao Wen, Jiekun Zeng, Yulin Huang, Xingguo Liu, and Kun Zhang

School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, Guangdong 510006, China

Supporting Information

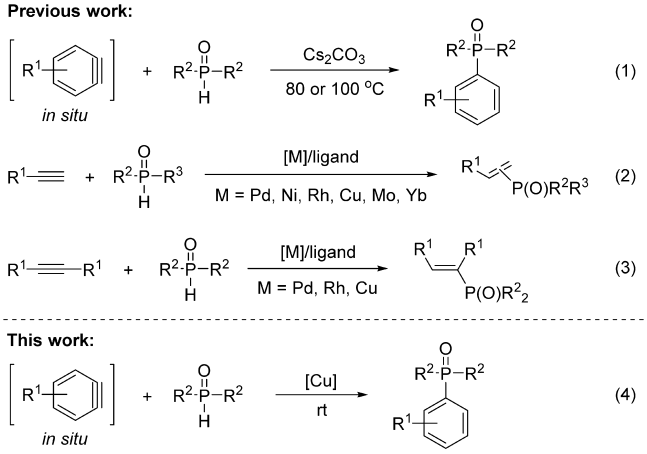


ABSTRACT: An efficient P-arylation of secondary phosphine oxides has been achieved through the ligand-free copper-catalyzed addition of H−P(O) bonds to *in situ* generated arynes at room temperature. This transformation provides a straightforward route to the formation of the aryl−P bond with wide functional group compatibility, which produces arylphosphine oxides in up to 99% yield.

Organophosphorus compounds have attracted much attention due to their wide applications in organic synthesis, medicinal chemistry, and material science.[1] Over the past few decades, a variety of useful synthetic methods for various organophosphorus compounds have been well-developed.[2] Currently, P-arylation has been of particular interest owning to the significant roles of arylphosphine complexes, which are the most important class of ligands in metal-catalyzed reactions.[3] The transition-metal-catalyzed Arbuzov or Hirao cross-coupling reaction of aryl halides with phosphorus nucleophiles provides an efficient P-arylation protocol for the synthesis of arylphosphonates and their derivatives,[4] while ligands, high temperatures, or long reaction times are generally required for the reaction conditions. On the other hand, the transition-metal-free C−P bond construction via the direct addition of phosphorus nucleophiles to arynes[5] is gradually developed.[6] Most recently, our group achieved the P-arylation of secondary phosphine oxides with arynes to synthesize arylphosphine oxides.[7] However, the reaction of $Ar_2P(O)H$ with arynes was realized at an elevated temperature (80 °C) with the assistance of excess Cs_2CO_3 (Scheme 1, eq 1). Simultaneously, the similar transformation under different reaction conditions was reported by Zhang and co-workers,[8] while the P-arylation of P(O)-H compounds was also achieved at 100 °C with excess Cs_2CO_3 (eq 1). Thus, an efficient methodology for the synthesis of important arylphosphine complexes based on readily available secondary phosphine oxides under ambient conditions is still a significant issue.

Since Han and co-workers invented the palladium-catalyzed hydrophosphorylation of alkynes in 1996,[9] various metal-catalyzed additions of a H−P(O) bond to the triple bond of terminal and internal alkynes have been well-documented using palladium,[10] nickel,[11] rhodium,[12] copper,[13] molybdenum,[14] and ytterbium[15] based catalysts (eqs 2 and 3), which provide a convenient method for the synthesis of alkenylphosphorus derivatives under mild conditions. To the best of our knowledge, transition-metal-catalyzed additions of a H−P(O) bond to *in situ* generated arynes remain unexplored. With our recent studies on the behaviors of arynes,[7,16] we have been interested in studying the addition of H−P(O) bonds to arynes catalyzed by the cheaper copper salts. Herein, we report that the utilization of CuI as the catalyst for the P-arylation of secondary phosphine oxides with arynes provides a convenient and general approach to arylphosphine oxides at room temperature.

Scheme 1. Overview of the Addition of H−P(O) Bonds to Triple Bonds



The reaction conditions were tested by using a model reaction between readily available *o*-silylphenyl triflate benzyne precursor **1a** and diphenylphosphine oxide **2a** with a variety of copper salts (10 mol %) in the presence of CsF in CH_3CN at room temperature, and the results are shown in Table 1. To our delight, the desired triphenylphosphine oxide **3aa** was obtained in 92% yield when $Cu(OAc)_2$ without additional ligands was

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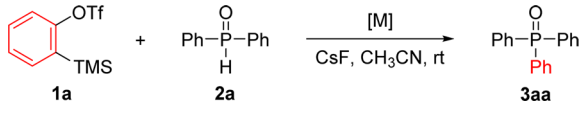
Table 1. Optimization of the Reaction Conditions[a]



entry	[M] (mol %)	yield of **3aa** (%)[b]
1		15
2	$Cu(OAc)_2$ (10)	92
3	$CuBr_2$ (10)	78
4	$CuSO_4$ (10)	45
5	CuOAc (10)	93
6	CuOTf (10)	85
7	CuCl (10)	93
8	CuBr (10)	76
9	CuI (10)	99
10	CuI (5)	99

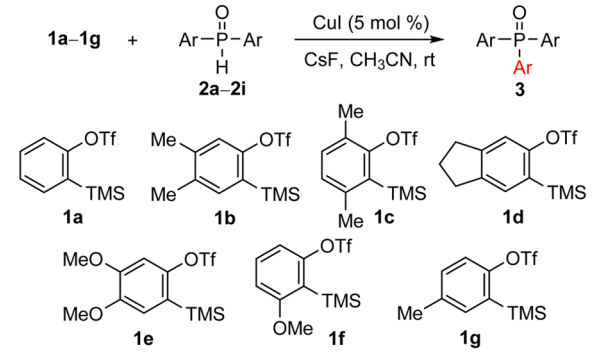
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), CsF (0.8 mmol) in CH_3CN (4 mL) stirring at room temperature under N_2 for 16 h. [b]Yield based on **1a** was determined by ^1H NMR analysis of crude products using an internal standard.

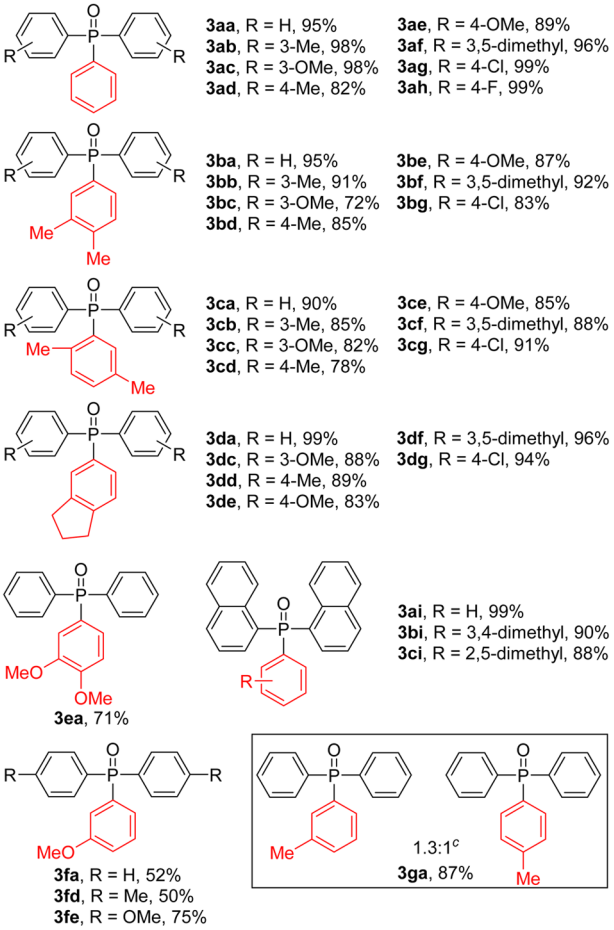
introduced (entry 2), while the reaction gave **3aa** in only 15% yield in the absence of the catalyst (entry 1).[7] Switching the copper salt from $Cu(OAc)_2$ to $CuBr_2$ or $CuSO_4$ significantly decreased the yield (entries 3 and 4). We then turned to screen copper(I) salts. CuOAc, CuOTf, CuCl, CuBr, and CuI showed good to high catalytic activities (entries 5–9), and CuI was proved to be the optimum catalyst (99% yield, entry 9). When the catalytic amount of CuI was decreased to 5 mol %, **3aa** was still obtained in 99% yield (entry 10). It is noteworthy that triphenylene generated by Cu(I)-catalyzed cyclotrimerization of benzyne[17] was not detected. Thus, we concluded that the optimized combination for the addition of H–P(O) bonds to arynes was to use 5 mol % of CuI as the catalyst, 4 equiv of CsF as the fluoride ion, and CH_3CN as the solvent, and the reaction was set at room temperature.

To investigate the scope of the P-arylation protocol, we applied the optimum conditions to the reaction of a variety of aryne precursors with various diarylphosphine oxides, and the results are illustrated in Table 2. Electron-rich and electron-poor $Ar_2P(O)H$ **2a–2i** were all well-tolerated for the P-arylation with arynes to smoothly produce the corresponding triarylphosphine oxides **3** in 50–99% yields. It is noteworthy that the P-arylation with 3,6-dimethyl-substituted aryne precursor **1c** afforded the sterically hindered triarylphosphine oxides **3ca–3cg** with *ortho*-methyl substitution in 78–91% yields, and the P-arylation of di(naphthalen-1-yl)phosphine oxide **2i** afforded the bulky triarylphosphine oxides **3ai**, **3bi**, and **3ci** in high yields. Unsymmetrical aryne precursors **1f** and **1g** were selected to study the regioselectivity of this arylation procedure. The 3-methoxy-substituted silylaryl triflate **1f** reacted cleanly with arynes to generate **3fa**, **3fd**, and **3fe** as a single isomer, which was in good agreement with the regioselectivity reported in the literature.[18] When 4-methyl-substituted silylaryl triflate **1g** was employed, two isomers were obtained (*meta*-**3ga**/*para*-**3ga** = 1.3:1), which further suggested that the reaction involved an aryne mechanism.

Having succeeded in the synthesis of triarylphosphine oxides, we then turned to the P-arylation of dialkylphosphine oxides with arynes (Scheme 2). To our delight, the reaction of dibutylphosphine oxide **2j** or dicyclopentylphosphine oxide **2k** with benzyne precursor **1a** under the same conditions smoothly

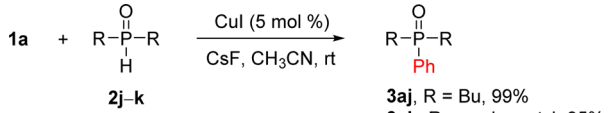
Table 2. Synthesis of Triarylphosphine Oxides[a,b]





[a]Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), CuI (0.01 mmol), CsF (0.8 mmol) in CH_3CN (4 mL) stirring at room temperature under N_2 for 16 h. [b]Isolated yield based on **1**. [c]Ratio was determined by ^1H NMR.

Scheme 2. Synthesis of Dialkylphenylphosphine Oxides



afforded the desired dialkylphenylphosphine oxide **3aj** or **3ak** in excellent yield. To illustrate the further synthetic utility of this method, the scale-up of the reaction of **1a** with diarylphosphine oxides was attempted. When we increased the scale of the

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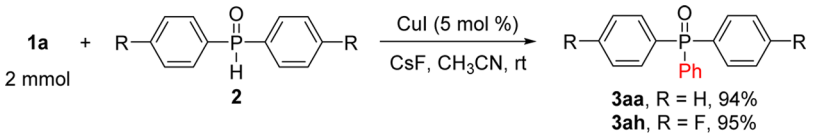
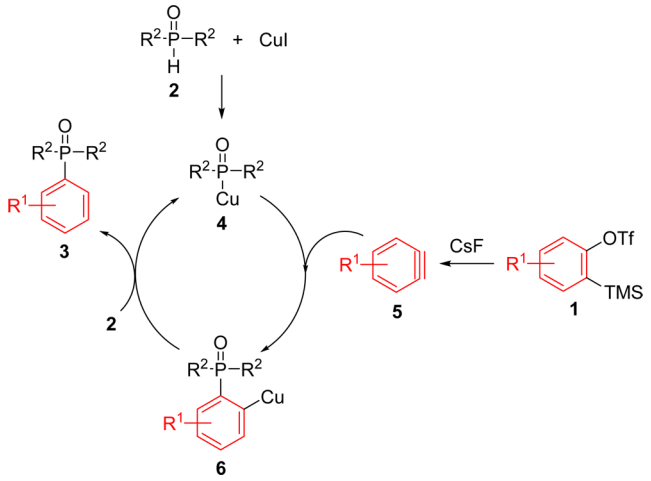
Scheme 3. Scale-Up of the Reaction



reaction from 0.2 to 2 mmol, the yields of **3aa** and **3ah** only slightly decreased (Scheme 3).

According to the experimental results and metal-catalyzed addition of H−P(O) bonds to alkynes,[9−15] a plausible mechanism for the copper-catalyzed addition of H−P(O) bonds to arynes is outlined in Scheme 4. CuI first reacts with

Scheme 4. Proposed Mechanism



secondary phosphine oxides **2** and forms the corresponding active [R^2_2P(O)Cu] intermediates **4**.[19] Insertion of *in situ* generated arynes **5** into the Cu−P bonds of **4** gives arylcopper intermediates **6**. Protonolysis of **6** by secondary phosphine oxides **2** results in arylphosphine oxides **3** and regenerates the active catalysts **4**. To further elucidate the mechanism of this reaction, the copper-catalyzed reaction of benzyne precursor **1a** with diphenylphosphine oxide in the presence of D_2O (2 equiv) afforded **3aa** in 83% yield with only 22% D incorporation at the *ortho*-position. As a comparison, our previous work shows that trace amounts of water serve as the proton source when the reaction was carried out without copper catalysts (Scheme 1, eq 1).[7] The difference between the two reactions suggests the formation of the arylcopper intermediate **6** from the intermediate **4** and benzyne **5**, which is mainly trapped by **2** leading to **3**.

In conclusion, we have developed a ligand-free copper-catalyzed addition of H−P(O) bonds to *in situ* generated arynes, which provides a highly efficient and convenient protocol for the synthesis of arylphosphine oxides with wide functional group compatibility under ambient conditions. To the best of our knowledge, this finding is the first example of transition-metal-catalyzed P-arylation of P(O)-H compounds with arynes. We envision that the reaction mode outlined here will have potential applications in organic synthesis.

EXPERIMENTAL SECTION

General Details. All reactions were carried out under an atmosphere of nitrogen using oven-dried glassware and standard syringe/septa techniques. Acetonitrile was distilled from calcium hydride. Petroleum ether refers to the petroleum fraction bp 40−60 °C. Commercial reagents were used without purification unless otherwise noted. Aryne precursors were prepared according to the literature.[20] Secondary phosphine oxides which were not commercially available were prepared according to the literature.[21] Flash chromatography was performed using the indicated solvent system on silica gel standard grade 60 (230−400 mesh). ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. ^{13}C NMR spectra were recorded on a 100 MHz spectrometer. ^{31}P NMR spectra were recorded on a 162 MHz spectrometer. ^{19}F NMR spectra were recorded on a 376 MHz spectrometer. Chemical shifts are reported relative to $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.16 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on ESI-TOF. The known compounds **3aa**,[7] **3ab**,[22] **3ad**,[7] **3ae**,[23] **3af**,[7] **3ah**,[23] **3aj**,[7] **3ak**,[7] **3ba**,[7] **3bd**,[7] **3bf**,[7] **3ca**,[7] **3cd**,[7] **3cf**,[7] **3ea**,[24] **3fa**,[6b] **3fe**,[25] and **3ga**[26] showed characterization data in full agreement with previously reported data.

General Procedure for the P-Arylation of Secondary Phosphine Oxides. To a solution of 2-(trimethylsilyl)phenyl triflate **1a** (60 mg, 0.2 mmol) and diphenylphosphine oxide **2a** (60 mg, 0.3 mmol) in acetonitrile (4 mL) were added CuI (2 mg, 0.01 mmol, 5 mol %) and CsF (116 mg, 0.8 mmol) under a nitrogen atmosphere. The mixture was stirred at room temperature for 16 h. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to give the pure product **3aa** (53 mg, 95%).

*Triphenylphosphine Oxide (**3aa**).* White amorphous solid (53 mg, 95%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.61 (m, 6H), 7.58−7.52 (m, 3H), 7.51−7.43 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.6 (d, J = 103 Hz), 132.0 (d, J = 9.9 Hz), 131.9 (d, J = 2.7 Hz), 128.5 (d, J = 12.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.1.

*Phenyldi-m-tolylphosphine Oxide (**3ab**).* White amorphous solid (60 mg, 98%):[22] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.62 (m, 2H), 7.56 (d, J = 12.4 Hz, 2H), 7.54−7.52 (m, 1H), 7.48−7.42 (m, 2H), 7.39−7.37 (m, 1H), 7.34−7.31 (m, 5H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4 (d, J = 12.0 Hz), 133.2 (d, J = 104 Hz), 132.8 (d, J = 103 Hz), 132.7 (d, J = 2.8 Hz), 132.5 (d, J = 9.5 Hz), 132.1 (d, J = 9.9 Hz), 131.8 (d, J = 2.7 Hz), 129.2 (d, J = 10.3 Hz), 128.3 (d, J = 4.7 Hz), 128.5 (d, J = 29.1 Hz), 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.6.

*Bis(3-methoxyphenyl)(phenyl)phosphine Oxide (**3ac**).* White amorphous solid (66 mg, 98%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.60 (m, 2H), 7.54 (t, J = 7.1 Hz, 1H), 7.50−7.40 (m, 2H), 7.40−7.31 (m, 2H), 7.28 (d, J = 13.1 Hz, 2H), 7.20−7.10 (m, 2H), 7.07 (d, J = 8.2 Hz, 2H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5 (d, J = 14.9 Hz), 133.6 (d, J = 104 Hz), 132.2 (d, J = 104 Hz), 132.0 (d, J = 10.0 Hz), 131.9 (d, J = 2.7 Hz), 129.6 (d, J = 14.4 Hz), 128.4 (d, J = 12.2 Hz), 124.3 (d, J = 10.1 Hz), 118.2 (d, J = 2.6 Hz), 116.8 (d, J = 10.8 Hz), 55.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.9; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{19}O_3PNa$ 361.0964; Found 361.0960.

*Phenyldi-p-tolylphosphine Oxide (**3ad**).* White amorphous solid (50 mg, 82%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66−7.61 (m, 2H), 7.55−7.47 (m, 5H), 7.43−7.39 (m, 2H), 7.23 (d, J = 6.6 Hz, 4H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3 (d, J = 2.6 Hz), 133.1 (d, J = 104 Hz), 132.3 (d, J = 10.2 Hz), 132.1 (d, J = 10.2 Hz), 131.8 (d, J = 2.5 Hz), 129.3 (d, J = 106 Hz), 129.2 (d, J = 12.5 Hz), 128.4 (d, J = 12.1 Hz), 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.3.

*Bis(4-methoxyphenyl)(phenyl)phosphine Oxide (**3ae**).* White amorphous solid (60 mg, 89%):[23] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.59 (m, 2H), 7.57−7.50 (m, 4H), 7.49−7.46 (m, 1H), 7.42−7.38 (m, 2H), 6.92 (dd, J = 8.9, 2.2 Hz, 4H), 3.79 (s, 6H); ^{13}C NMR

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(100 MHz, $CDCl_3$): δ 162.4 (d, J = 2.6 Hz), 134.0 (d, J = 11.2 Hz), 132.5 (d, J = 104 Hz), 132.0 (d, J = 10.1 Hz), 131.7 (d, J = 2.2 Hz), 128.4 (d, J = 12.8 Hz), 124.1 (d, J = 111 Hz), 114.1 (d, J = 13.1 Hz), 55.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.0.

*Bis(3,5-dimethylphenyl)(phenyl)phosphine Oxide (**3af**).* White amorphous solid (64 mg, 96%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.62 (m, 2H), 7.54−7.50 (m, 1H), 7.47−7.42 (m, 2H), 7.26 (d, J = 12.0 Hz, 4H), 7.16 (s, 2H), 2.31 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1 (d, J = 12.7 Hz), 133.6 (d, J = 2.8 Hz), 132.8 (d, J = 103 Hz), 132.1 (d, J = 104 Hz), 132.3 (d, J = 9.9 Hz), 131.9 (d, J = 2.7 Hz), 129.6 (d, J = 9.8 Hz), 128.3 (d, J = 12.0 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.7.

*Bis(4-chlorophenyl)(phenyl)phosphine Oxide (**3ag**).* White amorphous solid (69 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.53 (m, 7H), 7.52−7.39 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8 (d, J = 3.3 Hz), 133.4 (d, J = 10.8 Hz), 132.3 (d, J = 2.7 Hz), 131.9 (d, J = 10.0 Hz), 131.6 (d, J = 106 Hz), 130.7 (d, J = 106 Hz), 129.0 (d, J = 12.8 Hz), 128.7 (d, J = 12.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.7; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{13}Cl_2OPNa$ 368.9973; Found 368.9970.

*Bis(4-fluorophenyl)(phenyl)phosphine Oxide (**3ah**).* White amorphous solid (62 mg, 99%):[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.60 (m, 6H), 7.58−7.52 (m, 1H), 7.50−7.44 (m, 2H), 7.18−7.14 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1 (dd, $J_{C\text{-}F}$ = 254 Hz, $J_{C\text{-}P}$ = 3.1 Hz), 134.5 (dd, $J_{C\text{-}F}$ = 11.7 Hz, $J_{C\text{-}P}$ = 8.7 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.3 Hz), 132.2 (d, $J_{C\text{-}P}$ = 106 Hz), 132.1 (d, $J_{C\text{-}P}$ = 10.0 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.1 Hz), 128.5 (dd, $J_{C\text{-}P}$ = 108 Hz, $J_{C\text{-}F}$ = 3.0 Hz), 116.1 (dd, $J_{C\text{-}P}$ = 21.6 Hz, $J_{C\text{-}F}$ = 13.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ −106.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8.

*Di(naphthalen-1-yl)(phenyl)phosphine Oxide (**3ai**).* White amorphous solid (75 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.4 Hz, 2H), 7.93 (d, J = 7.9 Hz, 2H), 7.82 (d, J = 7.9 Hz, 2H), 7.63 (dd, J = 11.8, 7.6 Hz, 2H), 7.52−7.31 (m, 7H), 7.28−7.10 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0 (d, J = 2.8 Hz), 133.9 (d, J = 3.9 Hz), 133.5 (d, J = 12.0 Hz), 133.2 (d, J = 2.8 Hz), 132.3 (d, J = 9.8 Hz), 131.9 (d, J = 2.6 Hz), 129.5 (d, J = 102 Hz), 128.7, 128.6 (d, J = 12.3 Hz), 127.9 (d, J = 5.4 Hz), 126.9 (d, J = 86.7 Hz), 124.2 (d, J = 14.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{19}OPNa$ 401.1066; Found 401.1066.

*Dibutyl(phenyl)phosphine Oxide (**3aj**).* Thick oil (47 mg, 99%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.66 (m, 2H), 7.52−7.48 (m, 1H), 7.44−7.37 (m, 2H), 2.36 (br, 2H), 2.08−1.80 (m, 4H), 1.57−1.31 (m, 6H), 0.78 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.1 (d, J = 2.6 Hz), 131.1 (d, J = 126 Hz), 130.5 (d, J = 9.1 Hz), 128.7 (d, J = 11.4 Hz), 28.8 (d, J = 69.2 Hz), 23.9 (d, J = 15.3 Hz), 23.3 (d, J = 4.0 Hz), 13.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 44.8.

*Dicyclopentyl(phenyl)phosphine Oxide (**3ak**).* Thick oil (50 mg, 95%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72−7.68 (m, 2H), 7.51−7.46 (m, 1H), 7.42−7.38 (m, 2H), 2.36−2.28 (m, 2H), 2.01−1.76 (m, 4H), 1.70−1.41 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8 (d, J = 2.4 Hz), 131.3 (d, J = 2.4 Hz), 130.1 (d, J = 127 Hz), 128.3 (d, J = 10.7 Hz), 37.5 (d, J = 71.2 Hz), 27.0, 26.5 (d, J = 9.6 Hz), 26.0, 25.9 (d, J = 10.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.3.

*(3,4-Dimethylphenyl)diphenylphosphine Oxide (**3ba**).* White amorphous solid (58 mg, 95%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.63 (m, 4H), 7.55−7.49 (m, 3H), 7.47−7.42 (m, 4H), 7.32−7.27 (m, 1H), 7.2−7.19 (m, 1H), 2.30 (s, 3H), 2.27 (d, J = 7.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2 (d, J = 2.9 Hz), 137.2 (d, J = 12.3 Hz), 133.4 (d, J = 100 Hz), 133.0 (d, J = 9.8 Hz), 132.0 (d, J = 9.9 Hz), 131.9 (d, J = 2.7 Hz), 129.7 (d, J = 2.8 Hz), 129.9 (d, J = 110 Hz), 129.6, 128.5 (d, J = 12.1 Hz), 19.9, 19.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4.

*(3,4-Dimethylphenyl)di-m-tolylphosphine Oxide (**3bb**).* White amorphous solid (61 mg, 91%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.46 (m, 3H), 7.43−7.25 (m, 7H), 7.24−7.14 (m, 1H), 2.35 (s, 6H), 2.30 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0 (d, J = 2.9 Hz), 138.3 (d, J = 11.9 Hz), 137.0 (d, J = 12.3 Hz), 132.9 (d, J = 9.8 Hz), 132.8 (d, J = 103 Hz), 132.5 (d, J = 2.5 Hz), 132.4 (d, J = 11.9 Hz), 129.6 (d, J = 2.4 Hz), 129.6 (d, J = 109 Hz), 129.5 (d, J = 5.1 Hz), 129.1 (d, J = 10.2 Hz), 128.1 (d, J = 12.9 Hz), 21.4, 19.9, 19.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{23}OPNa$ 357.1379; Found 357.1377.

*(3,4-Dimethylphenyl)bis(3-methoxyphenyl)phosphine Oxide (**3bc**).* White amorphous solid (53 mg, 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 12.2 Hz, 1H), 7.46−7.29 (m, 5H), 7.28−7.14 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 3.85 (s, 6H), 2.36 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5 (d, J = 14.9 Hz), 141.2 (d, J = 2.9 Hz), 137.1 (d, J = 12.4 Hz), 134.1 (d, J = 103 Hz), 132.9 (d, J = 9.9 Hz), 129.7 (d, J = 4.4 Hz), 129.6 (d, J = 2.4 Hz), 129.5 (d, J = 14.2 Hz), 129.1 (d, J = 84.5 Hz), 124.3 (d, J = 10.1 Hz), 118.0 (d, J = 2.6 Hz), 116.7 (d, J = 10.7 Hz), 55.4, 19.9, 19.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{23}O_3PNa$ 389.1277; Found 389.1279.

*(3,4-Dimethylphenyl)di-p-tolylphosphine Oxide (**3bd**).* White amorphous solid (57 mg, 85%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.48 (m, 5H), 7.30−7.28 (m, 1H), 7.26−7.23 (m, 4H), 7.20−7.15 (m, 1H), 2.39 (s, 6H), 2.29 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1 (d, J = 2.5 Hz), 140.9 (d, J = 6.1 Hz), 137.0 (d, J = 12.2 Hz), 133.0 (d, J = 9.8 Hz), 132.1 (d, J = 10.2 Hz), 131.3 (d, J = 146 Hz), 130.5 (d, J = 106 Hz), 129.7 (d, J = 3.1 Hz), 129.5 (d, J = 6.0 Hz), 129.1 (d, J = 12.4 Hz), 21.6, 19.9, 19.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4.

*(3,4-Dimethylphenyl)bis(4-methoxyphenyl)phosphine Oxide (**3be**).* White amorphous solid (64 mg, 87%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 11.4, 8.7 Hz, 4H), 7.50−7.46 (m, 1H), 7.30−7.25 (m, 1H), 7.19−7.16 (m, 1H), 6.94 (dd, J = 8.7, 2.0 Hz, 4H), 3.83 (s, 6H), 2.29 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 2.7 Hz), 140.8 (d, J = 2.8 Hz), 136.9 (d, J = 12.3 Hz), 133.9 (d, J = 11.2 Hz), 132.9 (d, J = 9.8 Hz), 130.3 (d, J = 107 Hz), 129.6, 129.5 (d, J = 1.8 Hz), 124.5 (d, J = 110 Hz), 113.9 (d, J = 13.1 Hz), 55.3, 19.9, 19.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{23}O_3PNa$ 389.1277; Found 389.1279.

*(3,4-Dimethylphenyl)bis(3,5-dimethylphenyl)phosphine Oxide (**3bf**).* White amorphous solid (67 mg, 92%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 12.0 Hz, 1H), 7.31−7.25 (m, 5H), 7.20−7.17 (m, 1H), 7.14 (s, 2H), 2.31 (s, 15H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8 (d, J = 2.8 Hz), 138.0 (d, J = 12.7 Hz), 136.9 (d, J = 12.2 Hz), 133.4 (d, J = 2.8 Hz), 133.3 (d, J = 106 Hz), 133.0 (d, J = 9.6 Hz), 130.5 (d, J = 104 Hz), 129.6 (d, J = 9.8 Hz), 129.6 (d, J = 1.2 Hz), 128.7 (d, J = 11.4 Hz), 21.3, 19.9, 19.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.6.

*Bis(4-chlorophenyl)(3,4-dimethylphenyl)phosphine Oxide (**3bg**).* White amorphous solid (62 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.50 (m, 4H), 7.49−7.37 (m, 5H), 7.30−7.15 (m, 2H), 2.31 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 (d, J = 2.5 Hz), 138.6 (d, J = 3.1 Hz), 137.5 (d, J = 12.5 Hz), 133.4 (d, J = 10.7 Hz), 132.8 (d, J = 10.0 Hz), 131.1 (d, J = 105 Hz), 129.9 (d, J = 13.2 Hz), 129.5 (d, J = 10.3 Hz), 128.9 (d, J = 12.7 Hz), 128.5 (d, J = 119 Hz), 19.9, 19.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{17}Cl_2OPNa$ 397.0286; Found 397.0281.

*(3,4-Dimethylphenyl)di(naphthalen-1-yl)phosphine Oxide (**3bi**).* White amorphous solid (73 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 12.2 Hz, 1H), 7.58−7.44 (m, 4H), 7.41−7.24 (m, 5H), 7.22−7.14 (m, 1H), 2.34 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2 (d, J = 2.7 Hz), 137.2 (d, J = 12.4 Hz), 134.2, 134.1 (d, J = 18.1 Hz), 133.4 (d, J = 12.0 Hz), 133.3 (d, J = 9.6 Hz), 133.0 (d, J = 2.7 Hz), 130.2 (d, J = 106 Hz), 129.9 (d, J = 10.3 Hz), 129.7 (d, J = 78.1 Hz), 128.7, 128.0 (d, J = 5.4 Hz), 126.9 (d, J = 85.3 Hz), 124.2 (d, J = 14.4 Hz), 19.9, 19.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{28}H_{23}OPNa$ 429.1379; Found 429.1378.

*(2,5-Dimethylphenyl)diphenylphosphine Oxide (**3ca**).* White amorphous solid (55 mg, 90%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.62 (m, 4H), 7.56−7.51 (m, 2H), 7.48−7.43 (m, 4H), 7.22 (d, J = 7.8 Hz, 1H), 7.17−7.14 (m, 1H), 6.88 (d, J = 14.4 Hz, 1H), 2.36 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0 (d, J = 8.1 Hz), 134.7 (d, J = 12.8 Hz), 133.9 (d, J = 12.5 Hz), 132.9 (d, J = 104

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Hz), 132.8 (d, J = 2.7 Hz), 131.9 (d, J = 9.7 Hz), 131.8, 131.7 (d, J = 2.8 Hz), 130.4 (d, J = 103 Hz), 128.5 (d, J = 12.0 Hz), 21.2 (d, J = 4.7 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.7.

*(2,5-Dimethylphenyl)di-m-tolylphosphine Oxide (**3cb**).* White amorphous solid (57 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 12.3 Hz, 2H), 7.39−7.27 (m, 6H), 7.25−7.10 (m, 2H), 6.88 (d, J = 14.3 Hz, 1H), 2.37 (s, 9H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9 (d, J = 8.1 Hz), 138.4 (d, J = 11.9 Hz), 134.5 (d, J = 12.7 Hz), 133.9 (d, J = 12.6 Hz), 132.8 (d, J = 105 Hz), 132.6 (d, J = 2.6 Hz), 132.4 (d, J = 2.8 Hz), 132.3 (d, J = 9.2 Hz), 131.7 (d, J = 11.1 Hz), 130.6 (d, J = 102 Hz), 128.9 (d, J = 10.2 Hz), 128.2 (d, J = 12.9 Hz), 21.4, 21.2 (d, J = 4.6 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{23}OPNa$ 357.1379; Found 357.1377.

*(2,5-Dimethylphenyl)bis(3-methoxyphenyl)phosphine Oxide (**3cc**).* White amorphous solid (60 mg, 82%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.25 (m, 4H), 7.24−7.00 (m, 6H), 6.85 (d, J = 14.5 Hz, 1H), 3.80 (s, 6H), 2.38 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (d, J = 14.8 Hz), 140.0 (d, J = 8.0 Hz), 134.6 (d, J = 12.8 Hz), 134.1 (d, J = 103 Hz), 133.8 (d, J = 12.7 Hz), 132.8 (d, J = 2.6 Hz), 131.8 (d, J = 11.1 Hz), 130.2 (d, J = 104 Hz), 129.6 (d, J = 14.4 Hz), 124.1 (d, J = 10.0 Hz), 118.0 (d, J = 2.5 Hz), 116.6 (d, J = 10.5 Hz), 55.4, 21.1 (d, J = 4.7 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{23}O_3PNa$ 389.1277; Found 389.1279.

*(2,5-Dimethylphenyl)di-p-tolylphosphine Oxide (**3cd**).* White amorphous solid (52 mg, 78%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.49 (m, 4H), 7.27−7.24 (m, 4H), 7.21 (d, J = 7.7 Hz, 1H), 7.17−7.12 (m, 1H), 6.89 (d, J = 14.2 Hz, 1H), 2.40 (s, 6H), 2.36 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0 (d, J = 2.7 Hz), 139.9 (d, J = 8.1 Hz), 134.5 (d, J = 12.6 Hz), 133.9 (d, J = 12.5 Hz), 132.6 (d, J = 2.5 Hz), 131.9 (d, J = 10.1 Hz), 131.7 (d, J = 11.0 Hz), 130.9 (d, J = 102 Hz), 129.9 (d, J = 101 Hz), 129.2 (d, J = 12.4 Hz), 21.6, 21.2 (d, J = 4.6 Hz), 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.8.

*(2,5-Dimethylphenyl)bis(4-methoxyphenyl)phosphine Oxide (**3ce**).* White amorphous solid (62 mg, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 11.4, 8.7 Hz, 4H), 7.21−7.18 (m, 1H), 7.15−7.1 (m, 1H), 6.95 (dd, J = 8.7, 2.0 Hz, 4H), 6.88 (d, J = 14.3 Hz, 1H), 3.84 (s, 6H), 2.36 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, J = 2.8 Hz), 139.8 (d, J = 8.1 Hz), 134.5 (d, J = 12.7 Hz), 133.9 (d, J = 12.6 Hz), 133.7 (d, J = 11.1 Hz), 132.5 (d, J = 2.6 Hz), 131.7 (d, J = 11.1 Hz), 131.2 (d, J = 105 Hz), 124.4 (d, J = 110 Hz), 114.0 (d, J = 13.1 Hz), 55.3, 21.13 (d, J = 4.6 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{22}H_{23}O_3PNa$ 389.1277; Found 389.1279.

*(2,5-Dimethylphenyl)bis(3,5-dimethylphenyl)phosphine Oxide (**3cf**).* White amorphous solid (64 mg, 88%):[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.11 (m, 8H), 6.88 (d, J = 14.2 Hz, 1H), 2.36 (s, 3H), 2.31 (s, 6H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9 (d, J = 8.0 Hz), 138.0 (d, J = 12.6 Hz), 134.4 (d, J = 12.7 Hz), 133.9 (d, J = 12.6 Hz), 133.4 (d, J = 2.8 Hz), 132.3 (d, J = 102 Hz), 132.5 (d, J = 2.6 Hz), 131.6 (d, J = 11.0 Hz), 130.8 (d, J = 102 Hz), 129.4 (d, J = 9.7 Hz), 21.3, 21.2, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1.

*Bis(4-chlorophenyl)(2,5-dimethylphenyl)phosphine Oxide (**3cg**).* White amorphous solid (68 mg, 91%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.54 (m, 4H), 7.45 (d, J = 7.8 Hz, 4H), 7.25 (d, J = 8.5 Hz, 1H), 7.21−7.14 (m, 1H), 6.83 (d, J = 14.6 Hz, 1H), 2.36 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0 (d, J = 8.3 Hz), 138.5 (d, J = 3.3 Hz), 134.9 (d, J = 13.0 Hz), 133.6 (d, J = 12.8 Hz), 133.2 (d, J = 3.8 Hz), 133.2 (d, J = 10.5 Hz), 132.1 (d, J = 11.3 Hz), 131.2 (d, J = 104 Hz), 129.5 (d, J = 104 Hz), 129.0 (d, J = 12.7 Hz), 21.1 (d, J = 4.7 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.2; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{17}Cl_2OPNa$ 397.0286; Found 397.0281.

*(2,5-Dimethylphenyl)di(naphthalen-1-yl)phosphine Oxide (**3ci**).* White amorphous solid (72 mg, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 7.8 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H), 7.56−7.39 (m, 4H), 7.37−7.16 (m, 6H), 7.01 (d, J = 14.6 Hz, 1H), 2.42 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2 (d, J = 8.0 Hz), 135.0 (d, J = 12.8 Hz), 134.3 (d, J = 7.8 Hz), 134.0 (d, J = 1.3 Hz), 133.9 (d, J = 5.2 Hz), 133.3 (d, J = 12.0 Hz), 133.1 (d, J = 2.7 Hz), 132.8 (d, J = 2.6 Hz), 131.9 (d, J = 11.3 Hz), 130.6 (d, J = 102 Hz), 129.5 (d, J = 100 Hz), 128.7, 128.1 (d, J = 5.0 Hz), 126.9 (d, J = 83.9 Hz), 124.3 (d, J = 14.4 Hz), 21.5 (d, J = 3.9 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.6; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{28}H_{23}OPNa$ 429.1379; Found 429.1378.

*(2,3-Dihydro-1H-inden-5-yl)diphenylphosphine Oxide (**3da**).* White amorphous solid (63 mg, 99%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.63 (m, 4H), 7.57−7.50 (m, 3H), 7.47−7.42 (m, 4H), 7.41−7.36 (m, 1H), 7.30−7.28 (m, 1H), 3.10−2.82 (m, 4H), 2.22−1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9 (d, J = 2.7 Hz), 144.7 (d, J = 12.9 Hz), 133.0 (d, J = 104 Hz), 132.1 (d, J = 9.9 Hz), 131.7 (d, J = 2.6 Hz), 130.3 (d, J = 11.0 Hz), 129.7 (d, J = 99.1 Hz), 128.4 (d, J = 12.1 Hz), 127.9 (d, J = 10.2 Hz), 124.4 (d, J = 13.6 Hz), 32.8 (d, J = 33.2 Hz), 25.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.0; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{19}OPNa$ 341.1066; Found 341.1068.

*(2,3-Dihydro-1H-inden-5-yl)bis(3-methoxyphenyl)phosphine Oxide (**3dc**).* White amorphous solid (67 mg, 88%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 11.9 Hz, 1H), 7.36−7.17 (m, 6H), 7.11−7.03 (m, 2H), 6.99 (d, J = 7.9 Hz, 2H), 3.73 (s, 6H), 2.92−2.79 (m, 4H), 2.07−1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5 (d, J = 14.8 Hz), 149.0 (d, J = 2.2 Hz), 144.7 (d, J = 12.9 Hz), 134.2 (d, J = 103 Hz), 130.2 (d, J = 11.1 Hz), 129.6 (d, J = 106 Hz), 129.5 (d, J = 8.1 Hz), 127.8 (d, J = 10.2 Hz), 124.4 (d, J = 13.9 Hz), 124.4 (d, J = 10.0 Hz), 118.0 (d, J = 2.0 Hz), 116.8 (d, J = 10.6 Hz), 55.4, 32.9, 32.6, 25.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{23}H_{23}O_3PNa$ 401.1277; Found 401.1275.

*(2,3-Dihydro-1H-inden-5-yl)di-p-tolylphosphine Oxide (**3dd**).* White amorphous solid (62 mg, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.48 (m, 5H), 7.42−7.32 (m, 1H), 7.30−7.19 (m, 5H), 3.06−2.79 (m, 4H), 2.39 (s, 6H), 2.14−1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7 (d, J = 2.6 Hz), 144.6 (d, J = 12.8 Hz), 142.2 (d, J = 2.7 Hz), 132.1 (d, J = 10.2 Hz), 130.3 (d, J = 11.2 Hz), 130.1 (d, J = 105 Hz), 130.0 (d, J = 105 Hz), 129.1 (d, J = 12.0 Hz), 127.9 (d, J = 10.2 Hz), 124.4 (d, J = 13.6 Hz), 32.9, 32.6, 25.2, 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.5; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{23}H_{23}OPNa$ 369.1379; Found 369.1380.

*(2,3-Dihydro-1H-inden-5-yl)bis(4-methoxyphenyl)phosphine Oxide (**3de**).* White amorphous solid (63 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.49 (m, 5H), 7.40−7.32 (m, 1H), 7.27 (d, J = 6.6 Hz, 1H), 6.94 (d, J = 8.3 Hz, 4H), 3.83 (s, 6H), 3.03−2.79 (m, 4H), 2.17−1.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 2.8 Hz), 148.6 (d, J = 2.8 Hz), 144.6 (d, J = 12.8 Hz), 133.9 (d, J = 11.2 Hz), 130.6 (d, J = 104 Hz), 130.2 (d, J = 11.0 Hz), 127.8 (d, J = 10.2 Hz), 124.5 (d, J = 110 Hz), 124.3 (d, J = 13.5 Hz), 113.9 (d, J = 13.1 Hz), 55.3, 32.9, 32.6, 25.2 ; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.7; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{23}H_{23}O_3PNa$ 401.1277; Found 401.1275.

*(2,3-Dihydro-1H-inden-5-yl)bis(3,5-dimethylphenyl)phosphine Oxide (**3df**).* White amorphous solid (72 mg, 96%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 11.9 Hz, 1H), 7.42−7.33 (m, 1H), 7.28 (d, J = 12.3 Hz, 5H), 7.14 (s, 2H), 2.98−2.87 (m, 4H), 2.31 (s, 12H), 2.15−2.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6 (d, J = 2.7 Hz), 144.6 (d, J = 12.6 Hz), 137.9 (d, J = 12.7 Hz), 133.4 (d, J = 2.8 Hz), 132.8 (d, J = 103 Hz), 130.4 (d, J = 105 Hz), 130.2 (d, J = 11.0 Hz), 129.6 (d, J = 9.8 Hz), 127.9 (d, J = 10.1 Hz), 124.3 (d, J = 13.5 Hz), 32.9, 32.7, 25.2, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{25}H_{27}OPNa$ 397.1692; Found 397.1689.

*Bis(4-chlorophenyl)(2,3-dihydro-1H-inden-5-yl)phosphine Oxide (**3dg**).* White amorphous solid (73 mg, 94%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.55 (m, 4H), 7.49 (d, J = 12.2 Hz, 1H), 7.46−7.42 (m, 4H), 7.39−7.28 (m, 2H), 3.00−2.86 (m, 4H), 2.13−2.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5 (d, J = 2.7 Hz), 145.1 (d, J = 13.1 Hz), 138.6 (d, J = 3.3 Hz), 133.4 (d, J = 10.7 Hz), 131.2 (d, J = 105 Hz), 130.1 (d, J = 11.2 Hz), 129.4 (d, J = 107 Hz), 128.9 (d, J = 12.7 Hz), 127.7 (d, J = 10.4 Hz), 124.7 (d, J = 13.8 Hz), 33.0, 32.6,

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25.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}Cl_2OPNa$ 409.0286; Found 409.0281.

*(3,4-Dimethoxyphenyl)diphenylphosphine Oxide (**3ea**).* White amorphous solid (48 mg, 71%):[24] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.61 (m, 4H), 7.53 (d, J = 6.3 Hz, 2H), 7.48−7.43 (m, 4H), 7.30 (dd, J = 12.3, 1.4 Hz, 1H), 7.08−6.99 (m, 1H), 6.90 (d, J = 3.1 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (d, J = 1.4 Hz), 149.2 (d, J = 14.8 Hz), 132.6 (d, J = 105 Hz), 132.1 (d, J = 9.9 Hz), 131.9 (d, J = 2.6 Hz), 128.4 (d, J = 12.1 Hz), 125.9 (d, J = 11.3 Hz), 123.8 (d, J = 110 Hz), 114.2 (d, J = 11.5 Hz), 110.7 (d, J = 15.4 Hz), 56.1, 55.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.9.

*(3-Methoxyphenyl)diphenylphosphine Oxide (**3fa**).* White amorphous solid (32 mg, 52%):[6b] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.64 (m, 4H), 7.56−7.53 (m, 2H), 7.48−7.44 (m, 4H), 7.38−7.28 (m, 2H), 7.16−7.06 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6 (d, J = 15.0 Hz), 133.6 (d, J = 104 Hz), 132.3 (d, J = 104 Hz), 132.1 (d, J = 9.9 Hz), 131.9 (d, J = 2.6 Hz), 129.6 (d, J = 14.4 Hz), 128.5 (d, J = 12.1 Hz), 124.4 (d, J = 10.0 Hz), 118.2 (d, J = 3.0 Hz), 116.8 (d, J = 10.6 Hz), 55.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4.

*(3-Methoxyphenyl)di-p-tolylphosphine Oxide (**3fd**).* White amorphous solid (34 mg, 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 11.8, 8.0 Hz, 4H), 7.36−7.31 (m, 1H), 7.29−7.23 (m, 5H), 7.15−7.10 (m, 1H), 7.06−7.03 (m, 1H), 3.79 (s, 3H), 2.39 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5 (d, J = 14.8 Hz), 142.3 (d, J = 2.7 Hz), 134.4 (d, J = 103 Hz), 132.1 (d, J = 10.3 Hz), 129.9 (d, J = 106 Hz), 129.5 (d, J = 14.3 Hz), 129.2 (d, J = 12.5 Hz), 124.3 (d, J = 10.0 Hz), 118.0 (d, J = 2.6 Hz), 116.8 (d, J = 10.7 Hz), 55.4, 21.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{21}O_2PNa$ 359.1171; Found 359.1174.

*(3-Methoxyphenyl)bis(4-methoxyphenyl)phosphine Oxide (**3fe**).* White amorphous solid (55 mg, 75%):[25] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.51 (m, 4H), 7.38−7.22 (m, 2H), 7.16−7.02 (m, 2H), 6.96 (d, J = 8.1 Hz, 4H), 3.84 (s, 6H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 2.6 Hz), 159.6 (d, J = 14.8 Hz), 133.9 (d, J = 11.3 Hz), 132.5 (d, J = 101 Hz), 129.6 (d, J = 14.3 Hz), 124.4 (d, J = 111 Hz), 124.3 (d, J = 10.2 Hz), 118.0 (d, J = 2.4 Hz), 116.8 (d, J = 13.0 Hz), 114.1 (d, J = 13.2 Hz), 55.5, 55.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4.

*Diphenyl(m-tolyl)phosphine Oxide (meta-**3ga**) and Diphenyl(p-tolyl)phosphine Oxide (para-**3ga**).* White amorphous solid (51 mg, 87%):[26] two isomers in ∼1.3:1 ratio; ^{1}H NMR (400 MHz, $CDCl_3$) *meta*-**3ga**: δ 7.69−7.64 (m, 4H), 7.59−7.52 (m, 3H), 7.48−7.43 (m, 4H), 7.40−7.29 (m, 3H), 2.36 (s, 3H); *para*-**3ga**: δ 7.69−7.64 (m, 4H) 7.58−7.49 (m, 4H), 7.47−7.42 (m, 4H), 7.28−7.25 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *meta*-**3ga**: δ 138.5 (d, J = 11.9 Hz), 132.5 (d, J = 102 Hz), 132.8 (d, J = 2.7 Hz), 132.5 (d, J = 9.4 Hz), 132.1 (d, J = 103 Hz), 132.1 (d, J = 9.9 Hz), 131.9 (d, J = 2.7 Hz), 129.1 (d, J = 10.2 Hz), 128.5 (d, J = 12.1 Hz), 128.3 (d, J = 12.9 Hz), 21.4; *para*-**3ga**: δ 142.4 (d, J = 2.8 Hz), 132.7 (d, J = 103 Hz), 132.1 (d, J = 10.1 Hz), 132.0 (d, J = 9.8 Hz), 131.8 (d, J = 2.8 Hz), 129.2 (d, J = 12.4 Hz), 129.1 (d, J = 106 Hz), 128.4 (d, J = 12.0 Hz), 21.6 (d, J = 1.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) *meta*-**3ga**: δ 29.34; *para*-**3ga**: δ 29.29.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01776.

Copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra for **3** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: qianchen@gdut.edu.cn.

Notes

The authors declare no competing financial interest.

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