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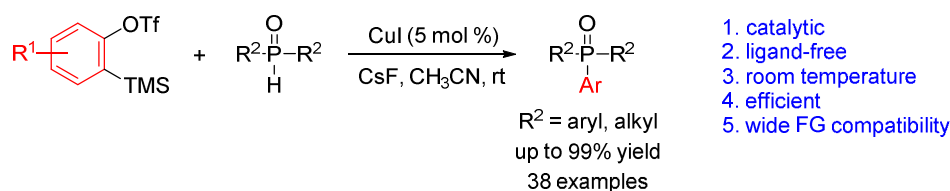
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Copper-Catalyzed Addition of H–P(O) Bonds to Arynes

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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.

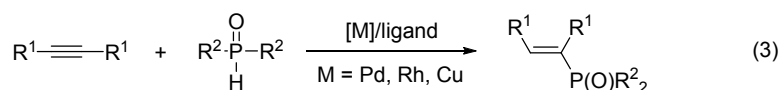
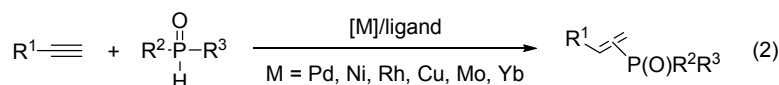
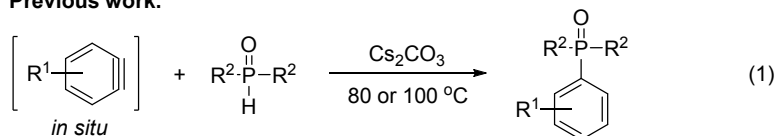
Organophosphorus compounds have attracted much attention due to their wide applications in organic synthesis, medicinal chemistry, and material science.¹ Over the past few decades, a variety of useful synthetic methods for various organophosphorus compounds have been well-developed.² Currently, P-arylation has been of particular interest owing 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 arynes⁵ 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 Ar₂P(O)H with arynes was realized at an elevated temperature (80 °C) with the assistance of excess Cs₂CO₃ (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 Cs₂CO₃ (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.

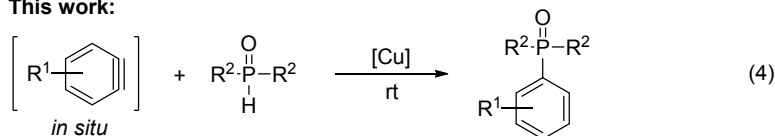
Since Han and co-workers invented the palladium-catalyzed hydrophosphorylation of alkynes in 1996,⁹ various metal-catalyzed additions of H–P(O) bond to the triple bond of terminal and internal alkynes have been well-documented using palladium,¹⁰ nickel,¹¹ rhodium,¹² copper,¹³ molybdenum,¹⁴ and ytterbium¹⁵ 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 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

Previous work:



This work:



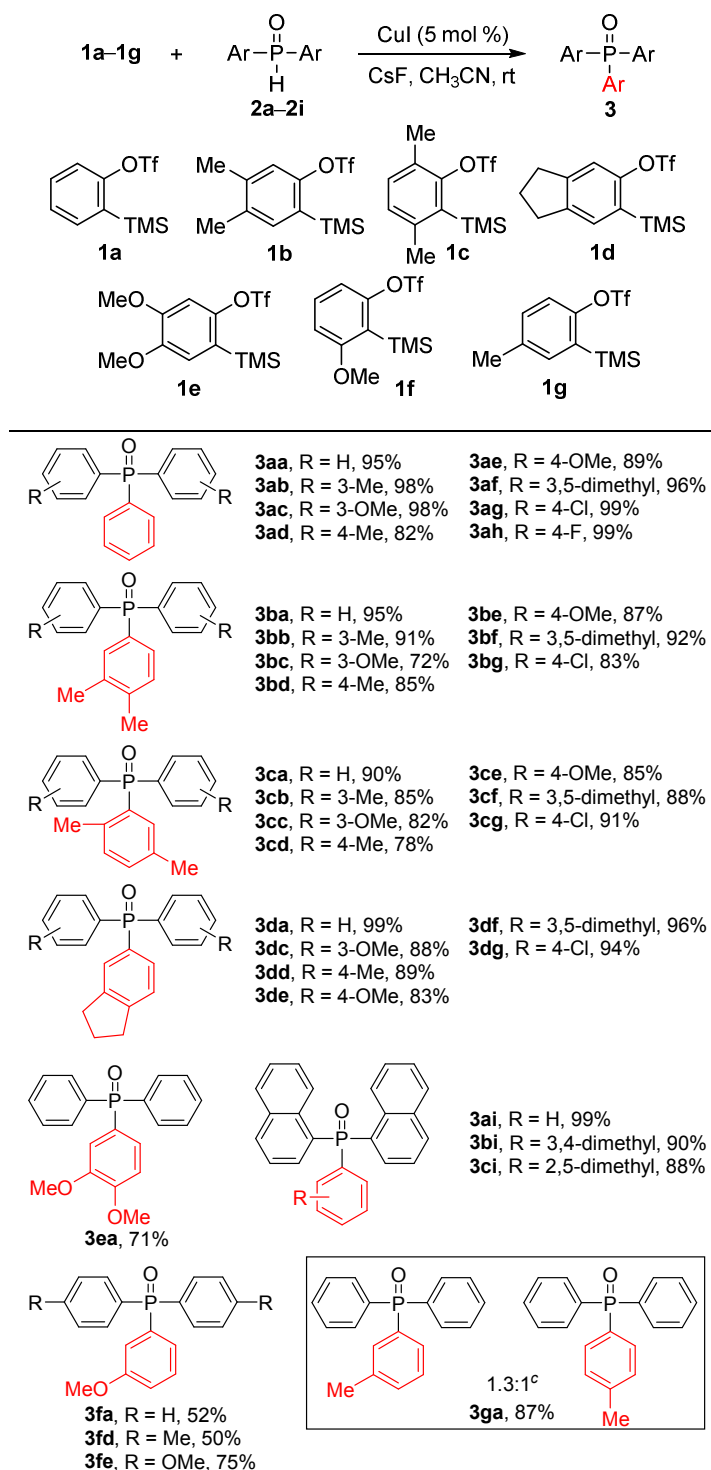
The reaction conditions were tested by using a model reaction between readily available *o*-silylphenyl triflate benzyne precursor **1a** and diphenylphosphine oxide **2a** with a variety of copper salts (10 mol %) in the presence of CsF in CH₃CN at room temperature, and the results were shown in Table 1. To our delight, the desired triphenylphosphine oxide **3aa** was obtained in 92% yield when Cu(OAc)₂ without additional ligands was 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 CuBr₂ or CuSO₄ 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 benzyne¹⁷ 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 CH₃CN as the solvent, and the reaction was set at room temperature.

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

^aReaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), CsF (0.8 mmol) in CH₃CN (4 mL) stirring at room temperature under N₂ for 16 h. ^bYield based on **1a** was determined by ¹H NMR analysis of crude products using an internal standard.

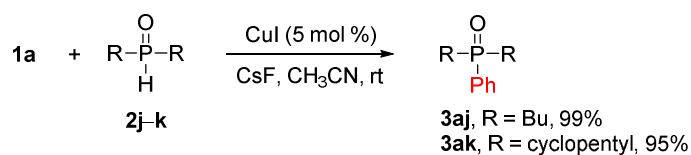
To investigate the scope of the P-arylation protocol, we applied the optimum conditions to the reaction of a variety of aryne precursors with various diarylphosphine oxides, and the results are illustrated in Table 2. Electron-rich and electron-poor Ar₂P(O)H **2a–2i** were all well tolerated for the 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.

Table 2. Synthesis of Triarylphosphine Oxides^{a,b}

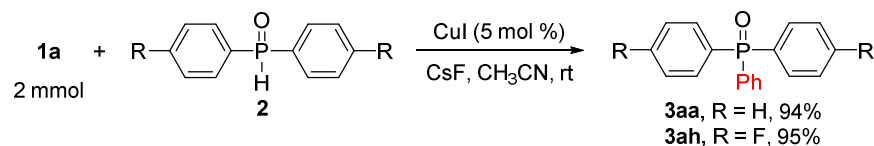
^aReaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), CuI (0.01 mmol), CsF (0.8 mmol) in CH_3CN (4 mL) stirring at room temperature under N_2 for 16 h. ^bIsolated yield based on **1**. ^cRatio was determined by ¹H NMR.

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

Scheme 2. Synthesis of Dialkylphenylphosphine Oxides



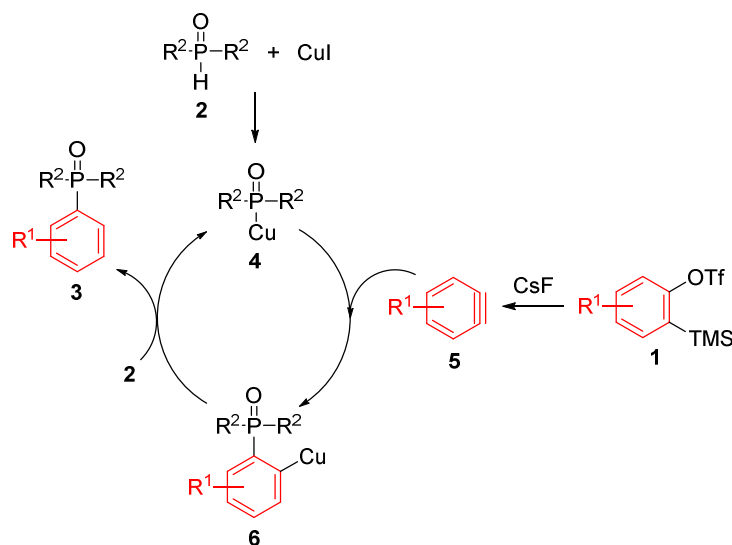
Scheme 3. Scale-up of the Reaction



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 secondary phosphine oxides **2** and forms the corresponding active $[\text{R}_2\text{P}(\text{O})\text{Cu}]$ 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 D₂O (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 serves 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**.

Scheme 4. Proposed Mechanism



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). ¹H NMR spectra were recorded on a 400 MHz spectrometer. ¹³C NMR spectra were recorded on a 100 MHz spectrometer. ³¹P NMR spectra were recorded on a 162 MHz spectrometer. ¹⁹F NMR spectra were recorded on a 376 MHz spectrometer. Chemical shifts are reported relative to CDCl₃ (δ 7.26 ppm) for ¹H NMR and CDCl₃ (δ 77.16 ppm) for ¹³C 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) was added CuI (2 mg, 0.01 mmol, 5 mol %) and CsF (116 mg, 0.8 mmol) under 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 ¹H NMR (400 MHz, CDCl₃) δ 7.68–7.61 (m, 6H), 7.58–7.52 (m, 3H), 7.51–7.43 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) 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); ³¹P NMR (162 MHz, CDCl₃) δ 29.1.

Phenyldi-*m*-tolylphosphine oxide (3ab). White amorphous solid (60 mg, 98%):²² ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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; ³¹P NMR (162 MHz, CDCl₃) δ 29.6.

Bis(3-methoxyphenyl)(phenyl)phosphine oxide (3ac). White amorphous solid (66 mg, 98%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_3\text{PNa}$ 361.0964; Found 361.0960.

Phenyldi-*p*-tolylphosphine oxide (3ad). White amorphous solid (50 mg, 82%): ^1H 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%): ^1H 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 (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%): ^1H 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%): ^1H 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,

CDCl₃) δ 27.7; HRMS (ESI-TOF) m/z : [M + Na]⁺ Calcd for C₁₈H₁₃Cl₂OPNa 368.9973; Found 368.9970.

Bis(4-fluorophenyl)(phenyl)phosphine oxide (3ah). White amorphous solid (62 mg, 99%):²³ ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 165.1 (dd, J_{C-F} = 254 Hz, J_{C-P} = 3.1 Hz), 134.5 (dd, J_{C-F} = 11.7 Hz, J_{C-P} = 8.7 Hz), 132.3 (d, J_{C-P} = 2.3 Hz), 132.2 (d, J_{C-P} = 106 Hz), 132.1 (d, J_{C-P} = 10.0 Hz), 128.8 (d, J_{C-P} = 12.1 Hz), 128.5 (dd, J_{C-P} = 108 Hz, J_{C-F} = 3.0 Hz), 116.1 (dd, J_{C-P} = 21.6 Hz, J_{C-F} = 13.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -106.3; ³¹P NMR (162 MHz, CDCl₃) δ 27.8.

Di(naphthalen-1-yl)(phenyl)phosphine oxide (3ai). White amorphous solid (75 mg, 99%): ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ³¹P NMR (162 MHz, CDCl₃) δ 36.3; HRMS (ESI-TOF) m/z : [M + Na]⁺ Calcd for C₂₆H₁₉OPNa 401.1066; Found 401.1066.

Dibutyl(phenyl)phosphine oxide (3aj). Thick oil (47 mg, 99%):⁷ ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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; ³¹P NMR (162 MHz, CDCl₃) δ 44.8.

Dicyclopentyl(phenyl)phosphine oxide (3ak). Thick oil (50 mg, 95%):⁷ ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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); ³¹P NMR (162 MHz, CDCl₃) δ 47.3.

(3,4-Dimethylphenyl)diphenylphosphine oxide (3ba). White amorphous solid (58 mg, 95%): ^1H 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%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{23}\text{OPNa}$ 357.1379; Found 357.1377.

(3,4-Dimethylphenyl)bis(3-methoxyphenyl)phosphine oxide (3bc). White amorphous solid (53 mg, 72%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{23}\text{O}_3\text{PNa}$ 389.1277; Found 389.1279.

(3,4-Dimethylphenyl)di-*p*-tolylphosphine oxide (3bd). White amorphous solid (57 mg, 85%): ^1H 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%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{23}\text{O}_3\text{PNa}$ 389.1277; Found 389.1279.

(3,4-Dimethylphenyl)bis(3,5-dimethylphenyl)phosphine oxide (3bf). White amorphous solid (67 mg, 92%): ^1H 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%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{OPNa}$ 397.0286; Found 397.0281.

(3,4-Dimethylphenyl)di(naphthalen-1-yl)phosphine oxide (3bi). White amorphous solid (73 mg, 90%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{23}\text{OPNa}$ 429.1379; Found 429.1378.

(2,5-Dimethylphenyl)diphenylphosphine oxide (3ca). White amorphous solid (55 mg, 90%): ^1H 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, $J = 104$ 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%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{23}\text{OPNa}$ 357.1379; Found 357.1377.

(2,5-Dimethylphenyl)bis(3-methoxyphenyl)phosphine oxide (3cc). White amorphous solid (60 mg, 82%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{23}\text{O}_3\text{PNa}$ 389.1277; Found 389.1279.

(2,5-Dimethylphenyl)di-*p*-tolylphosphine oxide (3cd). White amorphous solid (52 mg, 78%): ^1H 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, $J = 2.6$ 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{23}\text{OPNa}$ 357.1379; Found 357.1377.

= 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%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{23}\text{O}_3\text{PNa}$ 389.1277; Found 389.1279.

(2,5-Dimethylphenyl)bis(3,5-dimethylphenyl)phosphine oxide (3cf). White amorphous solid (64 mg, 88%): ^1H 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%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{17}\text{Cl}_2\text{OPNa}$ 397.0286; Found 397.0281.

(2,5-Dimethylphenyl)di(naphthalen-1-yl)phosphine oxide (3ci). White amorphous solid (72 mg, 88%): ^1H 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);

¹³C NMR (100 MHz, CDCl₃) 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; ³¹P NMR (162 MHz, CDCl₃) δ 38.6; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₈H₂₃OPNa 429.1379; Found 429.1378.

(2,3-Dihydro-1*H*-inden-5-yl)diphenylphosphine oxide (3da). White amorphous solid (63 mg, 99%): ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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; ³¹P NMR (162 MHz, CDCl₃) δ 30.0; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₁H₁₉OPNa 341.1066; Found 341.1068.

(2,3-Dihydro-1*H*-inden-5-yl)bis(3-methoxyphenyl)phosphine oxide (3dc). White amorphous solid (67 mg, 88%): ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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; ³¹P NMR (162 MHz, CDCl₃) δ 30.3; HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₃O₃PNa 401.1277; Found 401.1275.

(2,3-Dihydro-1*H*-inden-5-yl)di-*p*-tolylphosphine oxide (3dd). White amorphous solid (62 mg, 89%): ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{23}\text{OPNa}$ 369.1379; Found 369.1380.

(2,3-Dihydro-1*H*-inden-5-yl)bis(4-methoxyphenyl)phosphine oxide (3de). White amorphous solid (63 mg, 83%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{23}\text{O}_3\text{PNa}$ 401.1277; Found 401.1275.

(2,3-Dihydro-1*H*-inden-5-yl)bis(3,5-dimethylphenyl)phosphine oxide (3df). White amorphous solid (72 mg, 96%): ^1H 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 : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{27}\text{OPNa}$ 397.1692; Found 397.1689.

Bis(4-chlorophenyl)(2,3-dihydro-1*H*-inden-5-yl)phosphine oxide (3dg). White amorphous solid (73 mg, 94%): ^1H 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, 25.2; ^{31}P NMR (162 MHz, CDCl_3) δ 28.4; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{17}\text{Cl}_2\text{OPNa}$ 409.0286; Found 409.0281.

(3,4-Dimethoxyphenyl)diphenylphosphine oxide (3ea). White amorphous solid (48 mg, 71%): $^{24}^1\text{H}$ 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, CDCl₃) 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; ³¹P NMR (162 MHz, CDCl₃) δ 29.9.

(3-Methoxyphenyl)diphenylphosphine oxide (3fa). White amorphous solid (32 mg, 52%):^{6b} ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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; ³¹P NMR (162 MHz, CDCl₃) δ 29.4.

(3-Methoxyphenyl)di-*p*-tolylphosphine oxide (3fd). White amorphous solid (34 mg, 50%): ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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; ³¹P NMR (162 MHz, CDCl₃) δ 28.9; HRMS (ESI-TOF) m/z : [M + Na]⁺ Calcd for C₂₁H₂₁O₂PNa 359.1171; Found 359.1174.

(3-Methoxyphenyl)bis(4-methoxyphenyl)phosphine oxide (3fe). White amorphous solid (55 mg, 75%):²⁵ ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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; ³¹P NMR (162 MHz, CDCl₃) 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; ¹H NMR (400 MHz, CDCl₃) *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);

¹³C NMR (100 MHz, CDCl₃) *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); ³¹P NMR (162 MHz, CDCl₃) *meta*-**3ga**: δ 29.34; *para*-**3ga**: δ 29.29.

Supporting Information

Copies of ¹H, ¹³C and ³¹P NMR spectra for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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