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Graphical Abstract

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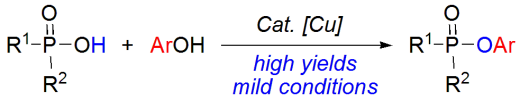
State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan Provincial Key Laboratory for Cost-effective Utilization of Fossil Fuel Aimed at Reducing Carbon-dioxide Emissions, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, P.R.China.



R^1 = aryl, alkoxyl, alkyl; R^2 = aryl, alkoxyl, alkyl

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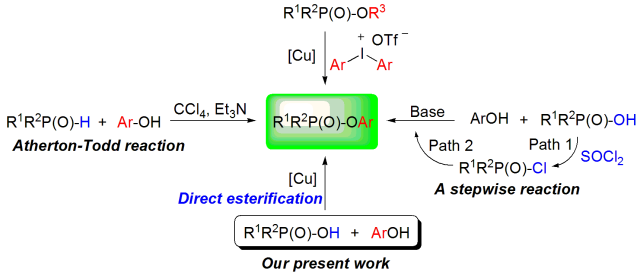
ABSTRACT

A novel copper-catalyzed method for the direct esterification of P(O)-OH compounds using phenols as efficient esterification reagents is illustrated. It is a simple way to generate a broad spectrum of functionalized *O*-aryl phosphinates, phosphonates, and phosphates from basic starting materials with moderate to excellent yields.

1. Introduction

Organophosphorus compounds are important intermediates in organic synthesis for the generation of industrial materials, medicinal chemicals, lubricants, and phosphine ligands,[1-6] showing a broad range of biological properties and acting as bioactive entitles. Certain phosphoryl esters are motifs in natural products, pharmacological agents, amino acid analogues, and synthetic precursors. In recent years, there is a growing interest in these kinds of compounds. For their preparation, orthodox nucleophlic substitution of toxic phosphorus halides with phenols are commonly adopted.[7] The reaction of P(O)-H compounds with phenols (the Atherton-Todd reaction) is also extensively used for the synthesis of the compounds, but the approach suffers from the low tolerance of functional groups and substrate limitations.[8] In 2014, FanÞanaìs-Mastral and Feringa first disclosed the synthesis of mixed alkyl aryl phosphonates using easily available phosphonates as starting materials over copper catalysts, where the P=O bond coordinates with copper efficiently to activate the phosphonates.[9]

So far, the direct cross-coupling of P(O)-OH compounds with iodobenzene or phenyl boronic acid has not been disclosed. We recently reported the reaction of P(O)-OH compounds with diaryl iodonium triflates for the synthesis of *O*-aryl organophosphorus compounds.[12k] As an ongoing effort on the activation of P(O)-OH compounds, we studied the direct esterification of P(O)-OH compounds with phenols under mild conditions using copper as catalyst. Herein we report this efficient and simple protocol that is more economical and convenient than those reported in the literature for the synthesis of *O*-aryl organophosphorus compounds without the use of diaryliodonium salts. Compared with P(O)-H or P-Cl compounds, P(O)-OH compounds are more air- and/or moisture-stable, and the use of them is more cost-saving and environment-benign. To the best of our knowledge, the synthesis of *O*-aryl organophosphorus compounds via the esterification of P(O)-OH compounds with phenols has not been realized.[10-12]



Scheme 1. Methods for the synthesis of *O*-aryl containing organophosphorus compounds.

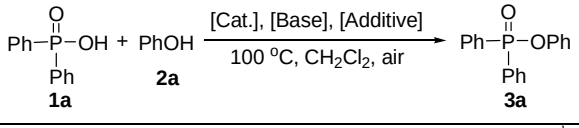
2. Results and Discussion

The reaction of diphenyl phosphinic acid with phenol at 100 ^{o}C with the assistance of CuI, CCl_4 and Et_3N in the presence of Na_2CO_3 under air atmosphere gives *O*-phenyl diphenyl phosphinate **3a** in 12% yield (Table 1, entry 1). The use of CCl_4 and Et_3N is crucial for the reaction. Among the copper sources (CuI, CuBr, CuCl, $CuBr_2$, $CuCl_2$, $Cu(OAc)_2$, CuO, Cu_2O, and Cu powder), Cu powder gives the best result (Table 1, entries 1-9). We investigated the effect of loading and found that when the

amount of Cu powder is increased from 10 to 20 mol%, the product yield increases from 23% to 43%, and a further increase of Cu powder to 50 mol% causes further increase to 91% (Table 1, entries 1, 9-11). Besides Na_2CO_3, we tested other bases such as K_2CO_3, *t*-BuONa, K_3PO_4, KOH, $NaHCO_3$ and AcOK. It is apparent that Na_2CO_3 is the best, and 91% yield of **3a** is obtained at a "diphenyl phosphinic acid:Na_2CO_3 molar ratio" of 1:2 (Table 1, entries 15-20).

Table 1

Optimization of the esterification of **1a** with **2a** [a]



1a **2a** **3a**

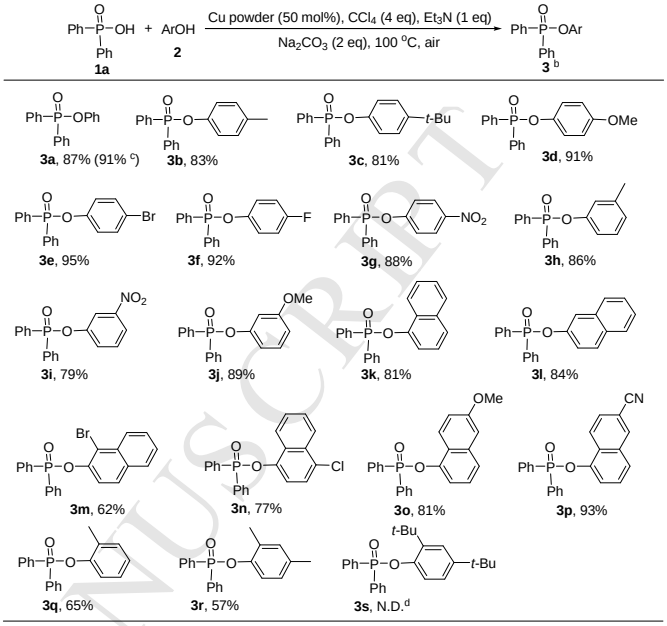
Entry	Catalyst (10 mol%)	Base	Yield [b]
1	CuI	Na_2CO_3	12%
2	CuBr	Na_2CO_3	9%
3	CuCl	Na_2CO_3	10%
4	$CuBr_2$	Na_2CO_3	9%
5	$CuCl_2$	Na_2CO_3	7%
6	$Cu(OAc)_2$	Na_2CO_3	7%
7	CuO	Na_2CO_3	5%
8	Cu_2O	Na_2CO_3	9%
9	Cu powder	Na_2CO_3	23%
10	Cu powder	Na_2CO_3	43% [c]
11	Cu powder	Na_2CO_3	91% [d]
12	Cu powder	Na_2CO_3	27% [e]
13	Cu powder	Na_2CO_3	66% [f]
14	Cu powder	Na_2CO_3	35% [g]
15	Cu powder	K_2CO_3	87%
16	Cu powder	*t*-BuONa	64%
17	Cu powder	K_3PO_4	73%
18	Cu powder	KOH	27%
19	Cu powder	$NaHCO_3$	89%
20	Cu powder	AcOK	trace
21	Cu powder	Na_2CO_3	29% [h]
22		Na_2CO_3	N.D. [i]

[a] Reactions were carried out with diphenyl phosphinic acid (0.5 mmol), phenol (1.0 mmol), Et_3N (0.5 mmol), CCl_4 (2.0 mmol), and base (1.0 mmol) in CH_2Cl_2 (3 mL), under air atmosphere stirred at 100 °C for 12 h. Entries 12-20, Cu powder (50 mol%). [b] Yield was determined by GC analysis, and dodecane was used as internal standard. [c] Cu powder (20 mol%). [d] Cu powder (50 mol%). [e] 60 °C. [f] 80 °C. [g] 120 °C. [h] No solvent used. [i] Copper powder (0 mol%), N.D. = Not detected.

It turned out that the copper-catalyzed esterification reaction is generally applicable for the transformation of P(O)-OH compounds to *O*-aryl organophosphorus compounds. As shown in Table 2, phenols such as *p*-cresol, 4-*tert*-butyl phenol, 4-methoxy phenol, 4-bromo phenol, 4-fluoro phenol, 4-nitro phenol, *m*-cresol, and 3-nitro phenol react efficiently with diphenyl phosphinic acid (**1a**) under the optimized reaction conditions to afford the corresponding products of *O*-aryl phosphoryl compounds **3** in moderate to excellent yields (Table 2, **3a**-**3i**). In addition, the reaction of **1a** with 3-methoxy phenol affords the desired product in 89% yield. It is observed that 1-naphthol and 2-naphthol also exhibit high reactivity, generating the corresponding products in 81% and 84% yields, respectively (Table 2, **3k**-**3l**). It was observed that substituted naphthols such as 1-bromo-2-naphthol, 4-chloro-1-naphtol, 6-methoxy-1-naphthol, and 6-cyano-1-naphtol give **3m**-**3p** in 62-93% yields. Ortho-substituted phenols such as 2-methyl phenol and 2,4-dimethyl phenol both react with diphenyl phosphinic acid efficiently, affording **3q** and **3r** in 65% and 57% yields. When 2,4-di-*tert*-butyl phenol was adopted for the reaction, the esterification product **3s** is not detected. And the phenomenon is plausibly due to steric hindrance. For most cases, electron-donating groups (Table 2, **3b**-**3d**, **3h**, **3j**, **3o**, **3q**-**3r**) or electron-withdrawing groups (Table 2, **3e**-**3g**, **3i**, **3m**-**3n** and **3p**) of phenols do not change the yields significantly.

Table 2

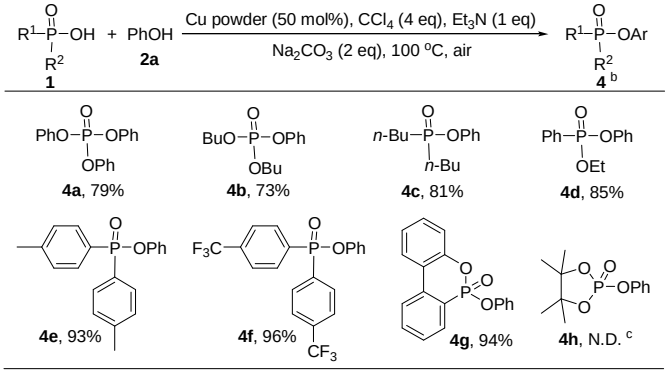
Scope of phenols [a]



[a] Reaction conditions: diphenyl phosphinic acid (0.5 mmol), phenols (1.0 mmol), Na_2CO_3 (1.0 mmol), Cu powder (50 mol%), CCl_4 (2.0 mmol), Et_3N (0.5 mmol), CH_2Cl_2 (3 mL), air, 100 °C, 12 h. [b] Isolated yields. [c] Yield was determined by GC analysis, and dodecane was used as internal standard. [d] N.D. = Not detected.

Table 3

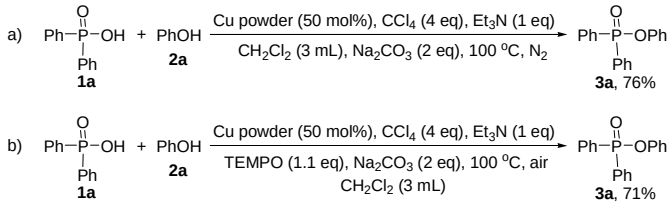
Scope of P(O)-OH compounds [a]



[a] Reaction conditions: P(O)-OH compounds (0.5 mmol), phenol (1.0 mmol), Na_2CO_3 (1.0 mmol), Cu powder (50 mol%), CCl_4 (2.0 mmol), Et_3N (0.5 mmol), CH_2Cl_2 (3 mL), air, 100 °C, 12 h. [b] Isolated yields. [c] N.D. = Not detected.

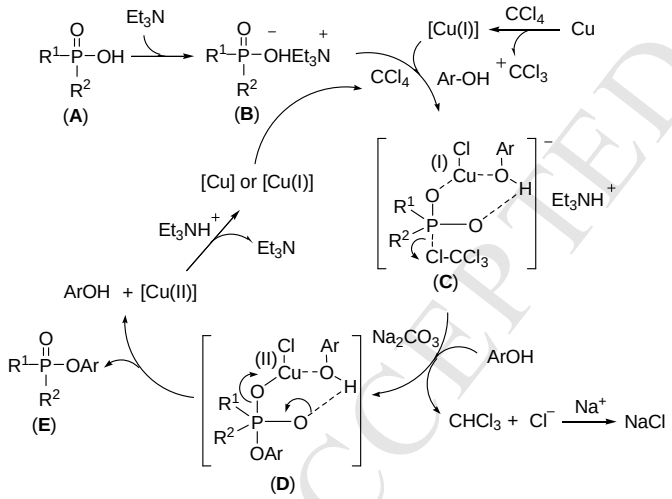
As depicted in Table 3, we investigated a variety of substituted P(O)-OH compounds (**1b**-**1i**) with phenol under the optimized conditions. It is clear that diphenyl hydrogen phosphate, dibutyl hydrogen phosphate, dibutyl phosphinic acid, and ethyl hydrogen phenylphosphonate react with phenol (**2a**) efficiently to give the corresponding *O*-aryl phosphoryl products **4a**-**4d** in 73-85% yields. Aryl substituted diphenyl phosphinic acids such as *di*-(4-methyl phenyl) phosphinic acid and *di*-(4-trifluoromethyl phenyl)

phosphinic acid are also good substrates for the reaction, and the expected esterification products of **4e** and **4f** are generated in 93% and 96% yields, respectively. In addition, *O*-phenyl-dibenzooxaphosphorine oxide **4g** is formed in 94% yield through the reaction of phenol with 10-hydroxy-9,10-dihydro-9-oxa-10-phosphaphenanthren-e-10-oxide. However, when a five-membered cyclic P(O)-OH compound (**1i)** is adopted, there is no detection of the corresponding esterification product. It is deduced that **1h** is unstable and plausibly undergoes decomposition under the adopted reaction conditions.



Scheme 2. Mechanistic investigation.

In order to clarify the reaction mechanism, we tested the effect of oxygen in this reaction. In a control reaction of diphenyl phosphinic acid with phenol under the same reaction conditions but in N_2 rather than in air, there is the generation of esterification product **3a** in 76% yield (Scheme 3, path a).[13] In addition, **3a** is also obtained in 71% yield with the addition of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) to the reaction. Thus, it is deduced that the reaction does not involve a step of radical interaction.



Scheme 3. Proposed mechanism.

A plausible mechanism for the copper-catalyzed esterification of P(O)-OH compounds with phenols is proposed as illustrated in Scheme 3.[12k, 14] P(O)-OH compound (**A**) first combines with Et_3N to form intermediate **B**. In the presence of CCl_4, copper powder is readily oxidized to the corresponding copper (I) salts. With the assistance of CCl_4, there is simultaneous coordination of intermediate **B** with Cu(I) and phenol, forming transition state **C** as a result. Then another molecule of phenol attacks **C** to give the copper (II) coordinated transition state **D** together with the elimination of $CHCl_3$ and Cl^-. Finally, the catalytic cycle is completed via the formation of P=O bond by means of elimination accompanied by the regeneration of Cu or Cu (I) as a catalytically active species.

3. Conclusion

In summary, we developed an efficient copper-catalyzed method for *O*-aryl esterification of P(O)-OH compounds with phenols through the activation of P=O double bond. The approach avoids the use of air-sensitive reagents, and the reaction can be performed under ambient conditions, making the experimental procedure simple. The synthetic method has high potential for the synthesis of biologically active molecules, catalytic ligands, and organophosphorus compounds.

4. Experimental section

4.1 General information and materials.

The reactions were conducted in a sealed Schlenk tube at 100 ^oC under N_2 or air atmosphere. All solvents used in reactions were freshly distilled. All other reagents were recrystallized or distilled as necessary. All reactions were performed under an atmosphere of dry nitrogen. The copper powder (99.9%, 231 um) and phenols (AR) adopted in the reaction were purchased from Aladdin Industrial Inc. ^1H (400 MHz), ^{13}C (100 MHz), and ^{31}P (162 MHz) spectra were recorded on a 400MHz spectrometer in $CDCl_3$. ^1H NMR chemical shifts are reported using TMS as internal standard; ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ as internal standard. The electron ionization method was used as the ionization method for the HRMS measurement, and the mass analyzer type is double-focusing.

4.2 General procedure.

A mixture of P(O)-OH compounds (0.5 mmol), Na_2CO_3 (1 mmol), CCl_4 (2 mmol), Et_3N (0.5 mmol) and Cu powder (0.25 mmol) in CH_2Cl_2 (3 mL) was stirred at 100 ^oC under air atmosphere for 12 h. Removal of the solvent under reduced pressure gave the crude product; pure product was obtained by passing the crude product through a short silica gel column using Hexane/EtOAc (1:1 to 5:1) as eluent

*4.2.1. O-phenyl phenyl (phenyl) phosphinate (**3a**).*[12k] Yield: 127.8 mg, (87 %). Yellow oil. ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS): δ= 7.87-7.92 (m, 4H; Ar), 7.49-7.53 (m, 2H; Ar), 7.42-7.46 (m, 4H; Ar), 7.19-7.26 (m, 4H; Ar), 7.04-7.07 (m, 1H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^oC, TMS): δ= 150.9 (d, ^1J (C,P) = 8.1 Hz; Ar), 132.5 (d, ^1J (C,P) = 2.8 Hz; Ar), 131.8 (d, ^1J (C,P) = 10.4 Hz; Ar), 131.0 (d, ^1J (C,P) = 137.4 Hz; Ar-C-P), 129.7 (s; Ar), 128.6 (d, ^1J (C,P) = 13.4 Hz; Ar), 124.6 (s; Ar), 120.7 (d, ^1J (C,P) = 4.8 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^oC): δ= 30.38.

*4.2.2. 4-Methyl-O-phenyl phenyl (phenyl) phosphinate (**3b**).*[12k] Yield: 127.6 mg, (83 %). Yellow oil. ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS): δ= 7.86-7.92 (m, 4H; Ar), 7.47-7.53 (m, 2H; Ar), 7.44-7.47 (m, 4H; Ar), 7.06-7.09 (m, 2H; Ar), 7.00-7.03 (m, 2H; Ar), 2.24 (s, 3H; -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^oC, TMS): δ= 148.4 (d, ^1J (C,P) = 8.1 Hz; Ar), 134.0 (s; Ar), 132.3 (s; Ar), 131.7 (d, ^1J (C,P) = 10.2 Hz; Ar), 130.9 (d, ^1J (C,P) = 139.0 Hz; Ar-C-P), 130.0 (s; Ar), 128.4 (d, ^1J (C,P) = 13.4 Hz; Ar), 120.3 (d, ^1J (C,P) = 3.7 Hz; Ar), 20.6 (s; -CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^oC): δ= 28.06.

*4.2.3. 4-tert-Butyl-O-phenyl phenyl (phenyl) phosphinate (**3c**).*[12k] Yield: 141.7 mg, (81 %). White solid. ^1H NMR (400 MHz, $CDCl_3$, 25 ^oC, TMS): δ= 7.78-7.84 (m, 4H; Ar), 7.36-7.42 (m, 2H; Ar), 7.33-7.36 (m, 4H; Ar), 7.14 (d, J = 8.4 Hz, 2H; Ar), 1.15 (s, 9H; -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^oC, TMS): δ= 148.3 (d, ^1J (C,P) = 8.3 Hz; Ar), 147.2 (s; Ar), 132.2 (d, ^1J (C,P) = 2.3 Hz; Ar), 131.6 (d, ^1J (C,P) = 7.8 Hz; Ar), 131.1 (d, ^1J (C,P)

= 137.3 Hz; Ar-C-P), 128.4 (d, ^{1}J (C,P) = 13.3 Hz; Ar), 126.4 (s; Ar), 119.9 (d, ^{1}J (C,P) = 4.6 Hz; Ar), 34.1 (s; -C-(CH_3)$_3$), 31.2 (s; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 31.27.

*4.2.4. 4-Methoxy-O-phenyl phenyl (phenyl) phosphinate (**3d**).* [12k] Yield: 147.1 mg, (91 %). White solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.86-7.91 (m, 4H; Ar), 7.48-7.55 (m, 2H; Ar), 7.43-7.47 (m, 4H; Ar), 7.10 (d, J = 11.2 Hz, 2H; Ar), 6.74 (d, J = 11.2 Hz, 2H; Ar), 3.71 (s, 3H; OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 156.1 (s; Ar), 144.0 (d, ^{1}J (C,P) = 8.2 Hz; Ar), 132.1 (d, ^{1}J (C,P) = 2.4 Hz; Ar), 131.5 (d, ^{1}J (C,P) = 10.5 Hz; Ar),130.7 (d, ^{1}J (C,P) = 137.1 Hz; Ar-C-P), 128.3 (d, ^{1}J (C,P) = 13.3 Hz; Ar), 121.3 (d, ^{1}J (C,P) = 4.3 Hz; Ar), 114.3 (s; Ar), 55.1 (d, ^{1}J (C,P) = 4.2 Hz; OCH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 28.44.

*4.2.5. 4-Bromo-O-phenyl phenyl (phenyl) phosphinate (**3e**).* [12k] Yield: 177.5 mg mg, (95 %). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.85-7.90 (m, 4H; Ar), 7.52-7.54 (m, 2H; Ar), 7.44-7.48 (m, 4H; Ar), 7.32-7.34 (m, 2H; Ar), 7.09-7.11 (m, 2H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 149.8 (d, ^{1}J (C,P) = 7.9 Hz; Ar), 132.6 (s; Ar), 132.5 (s; Ar), 131.6 (d, ^{1}J (C,P) = 10.4 Hz; Ar), 130.3 (d, ^{1}J (C,P) = 137.1 Hz; Ar-C-P), 128.6 (d, ^{1}J (C,P) = 13.4 Hz; Ar), 122.4 (d, ^{1}J (C,P) = 4.6 Hz; Ar), 117.5 (s; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 29.16.

*4.2.6. 4-Fluoro-O-phenyl phenyl (phenyl) phosphinate (**3f**).* [12k] Yield: 143.8 mg, (92 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.85-7.90 (m, 4H; Ar), 7.52-7.54 (m, 2H; Ar), 7.46-7.49 (m, 4H; Ar), 7.13-7.15 (m, 2H; Ar), 6.69-6.93 (m, 2H ; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 159.5 (d, ^{2}J (C,F) = 241.8 Hz; Ar-C-F), 146.7 (d, ^{1}J (C,P) = 5.6 Hz; Ar), 132.6 (d, ^{1}J (C,P) = 2.4 Hz; Ar), 131.8 (d, ^{1}J (C,P) = 10.3 Hz; Ar), 130.7 (d, ^{1}J (C,P) = 137.1 Hz; Ar-C-P), 128.7 (d, ^{1}J (C,P) = 13.4 Hz; Ar), 122.2 (dd, ^{1}J (C,P) = 3.7 Hz, ^{2}J (C,F) = 12.7 Hz; Ar), 116.2 (d, ^{1}J (C,P) = 23.2 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 29.05; ^{19}F NMR (377 MHz, $CDCl_3$, 25 ^{o}C): δ= -118.3.

*4.2.7. 4-Nitro-O-phenyl phenyl (phenyl) phosphinate (**3g**).* [15a] Yield: 175.9 mg, (88 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.13-8.15 (m, 2H; Ar), 7.86-7.91 (m, 4H; Ar), 7.58-7.59 (m, 2H; Ar), 7.49-7.52 (m, 4H; Ar), 7.37-7.39 (m, 2H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 155.8 (d, ^{1}J (C,P) = 7.5 Hz; Ar), 144.2 (s; Ar), 132.9 (s; Ar), 131.5 (d, ^{1}J (C,P) = 10.6 Hz; Ar), 129.7 (d, ^{1}J (C,P) = 137.3 Hz; Ar-C-P), 128.7 (d, ^{1}J (C,P) = 13.6 Hz; Ar), 125.5 (s; Ar), 121.1 (d, ^{1}J (C,P) = 5.0 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 30.49.

*4.2.8. 3-Methyl-O-phenyl phenyl (phenyl) phosphinate (**3h**).* [15b] Yield: 132.4 mg, (86 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.86-7.92 (m, 4H; Ar), 7.49-7.53 (m, 2H; Ar), 7.42-7.47 (m, 4H; Ar), 7.05-7.11 (m, 2H; Ar), 6.96-6.98 (m, 1H; Ar), 6.86-6.88 (m, 1H; Ar), 2.25 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 150.7 (d, ^{1}J (C,P) = 8.1 Hz; Ar), 139.7 (s; Ar), 132.3 (s; Ar), 131.7 (d, ^{1}J (C,P) = 10.2 Hz; Ar), 131.1 (d, ^{1}J (C,P) = 174.2 Hz; Ar-C-P), 129.2 (s; Ar), 128.4 (d, ^{1}J (C,P) = 13.4 Hz; Ar), 125.3 (s; Ar), 121.2 (d, ^{1}J (C,P) = 4.6 Hz; Ar), 117.4 (d, ^{1}J (C,P) = 4.6 Hz; Ar), 21.2 (s; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 27.97.

*4.2.9. 3-Nitro-O-phenyl phenyl (phenyl) phosphinate (**3i**).* [15a] Yield: 134.2 mg, (79 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.88-8.02 (m, 6H; Ar), 7.63-7.66 (m, 1H; Ar), 7.56-7.61 (m, 2H; Ar), 7.48-7.53 (m, 4H; Ar), 7.41-7.45 (m, 1H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 151.1 (d, ^{1}J (C,P) = 7.4 Hz; Ar), 148.7 (s; Ar), 132.9 (s; Ar), 131.6 (d, ^{1}J (C,P) = 10.6 Hz; Ar), 130.2 (s; Ar), 129.8 (d, ^{1}J (C,P) = 137.0 Hz; Ar), 128.7 (d, ^{1}J (C,P) = 13.5 Hz; Ar), 127.0 (d, ^{1}J (C,P) = 4.0 Hz; Ar), 119.5 (s; Ar), 116.1 (d, ^{1}J (C,P) = 5.1 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 30.63.

*4.2.10. 3-Methoxy-O-phenyl phenyl (phenyl) phosphinate (**3j**).* [15c] Yield: 140.6 mg, (89 %). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.87-7.92 (m, 4H; Ar), 7.43-7.54 (m, 6H; Ar), 7.09-7.13 (m, 1H; Ar), 6.78-6.80 (m, 2H; Ar), 6.61-6.63 (m, 1H; Ar), 3.70 (s, 3H; OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 160.6 (s; Ar), 132.5 (d, ^{1}J (C,P) = 2.9 Hz; Ar), 131.8 (d, ^{1}J (C,P) = 10.3 Hz; Ar), 130.9 (d, ^{1}J (C,P) = 137.5 Hz; Ar-C-P), 130.0 (s; Ar), 128.7 (s; Ar), 128.6 (s; Ar), 112.9 (d, ^{1}J (C,P) = 4.8 Hz; Ar), 110.7 (s; Ar), 106.7 (d, ^{1}J (C,P) = 5.2 Hz; Ar), 55.3 (s; OCH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 30.42.

*4.2.11. O-Naphthalen-1-yl phenyl (phenyl) phosphinate (**3k**).* [15d] Yield: 139.4 mg, (81 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.20-8.22 (m, 1H; Ar), 7.94-7.99 (m, 4H; Ar), 7.78-7.80 (m, 1H; Ar), 7.44-7.54 (m, 10H; Ar), 7.23-7.27 (m, 1H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 171.2 (s; Ar), 147.1 (d, ^{1}J (C,P) = 8.3 Hz; Ar), 134.8 (s; Ar), 132.6 (d, ^{1}J (C,P) = 2.7 Hz; Ar), 131.7 (d, ^{1}J (C,P) = 10.4 Hz; Ar), 131.0 (d, ^{1}J (C,P) = 137.8 Hz; Ar-C-P), 128.7 (d, ^{1}J (C,P) = 3.4 Hz; Ar), 127.9 (s; Ar), 126.6 (s; Ar), 126.5 (s; Ar), 125.6 (s; Ar), 124.4 (s; Ar), 121.6 (s; Ar), 115.3 (d, ^{1}J (C,P) = 4.4 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 30.97.

*4.2.12. O-Naphthalen-2-yl phenyl (phenyl) phosphinate (**3l**).* Yield: 144.8 mg, (84 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.93-7.98 (m, 4H; Ar), 7.71-7.76 (m, 4H; Ar), 7.38-7.53 (m, 9H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 148.5 (d, ^{1}J (C,P) = 8.2 Hz; Ar), 133.8 (s; Ar), 132.4 (s; Ar), 131.8 (s; Ar), 131.7 (s; Ar), 130.7 (d, ^{1}J (C,P) = 137.6 Hz; Ar-C-P), 130.5 (s; Ar), 129.6 (s; Ar), 128.5 (d, ^{1}J (C,P) = 13.4 Hz; Ar), 127.4 (d, ^{1}J (C,P) = 10.5 Hz; Ar), 126.4 (s; Ar), 125.1 (s; Ar), 120.6 (d, ^{1}J (C,P) = 4.7 Hz; Ar), 117.1 (d, ^{1}J (C,P) = 4.9 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 28.63. HRMS calcd. for $C_{22}H_{17}O_2P$: 344.0966, found: 344.0963.

*4.2.13. O-1-Bromonaphthalen-2-yl phenyl (phenyl) phosphinate (**3m**).* [15e] Yield: 131.1 mg, (62 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.20-8.22 (m, 1H; Ar), 8.02-8.08 (m, 4H; Ar), 7.85-7.87 (m, 1H; Ar), 7.67-7.76 (m, 2H; Ar), 7.42-7.58 (m, 8H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 146.8 (d, ^{1}J (C,P) = 7.2 Hz; Ar), 132.7 (d, ^{1}J (C,P) = 2.9 Hz; Ar), 132.1 (d, ^{1}J (C,P) = 145.6 Hz; Ar-C-P), 132.0 (d, ^{1}J (C,P) = 10.6 Hz; Ar), 131.3 (s; Ar), 130.0 (s; Ar), 129.0 (s; Ar), 128.7 (d, ^{1}J (C,P) = 13.6 Hz; Ar), 128.2 (s; Ar), 127.8 (s; Ar), 126.7 (s; Ar), 125.8 (s; Ar), 120.5 (d, ^{1}J (C,P) = 3.5 Hz; Ar), 112.5 (d, ^{1}J (C,P) = 7.6 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.04.

*4.2.14. O-1-Chloronaphthalen-4-yl phenyl (phenyl) phosphinate (**3n**).* Yield: 145.9 mg, (77 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.19-8.24 (m, 2H; Ar), 7.92-7.97 (m, 4H; Ar), 7.34-7.63 (m, 10H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 146.1 (d, ^{1}J (C,P) = 8.2 Hz; Ar), 132.7 (d, ^{1}J (C,P) = 2.9 Hz; Ar), 131.8 (d, ^{1}J (C,P) = 10.4 Hz; Ar), 131.7 (s; Ar), 130.7 (d, ^{1}J (C,P) = 137.4 Hz; Ar-C-P), 128.9 (s; Ar), 128.7 (s; Ar), 127.7 (s; Ar), 127.6 (s; Ar), 127.0 (s; Ar), 125.7 (s; Ar), 124.7 (s; Ar), 122.1 (s; Ar), 115.3 (d, ^{1}J (C,P) = 4.3 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 31.63. HRMS calcd. for $C_{22}H_{16}ClO_2P$: 378.0576, found: 378.0574.

*4.2.15. O-2-Methoxynaphthalen-5-yl phenyl (phenyl) phosphinate (**3o**).* Yield: 151.1 mg, (81 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.90-7.95 (m, 4H; Ar), 7.58-7.61 (m, 3H; Ar), 7.42-7.52 (m, 6H; Ar), 7.30-7.33 (m, 1H; Ar), 7.03-7.10 (m, 2H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 157.3 (s; Ar), 146.9 (d, ^{1}J (C,P) = 8.4 Hz; Ar), 132.5 (d, ^{1}J (C,P) = 2.9 Hz; Ar), 131.8 (d, ^{1}J (C,P) = 10.3 Hz; Ar),

131.7 (s; Ar), 131.0 (d, ^{1}J (C,P) = 137.4 Hz; Ar-C-P), 129.2 (s; Ar), 128.9 (s; Ar), 128.6 (d, ^{1}J (C,P) = 13.4 Hz; Ar),, 128.4 (s; Ar), 121.1 (d, ^{1}J (C,P) = 4.8 Hz; Ar), 119.4 (s; Ar), 117.3 (d, ^{1}J (C,P) = 5.0 Hz; Ar), 105.7 (s; Ar), 55.3 (s; OCH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 30.70. HRMS calcd. for $C_{23}H_{19}O_3P$: 374.1072, found: 374.1069.

*4.2.16. O-2-Cyanonaphthalen-5-yl phenyl (phenyl) phosphinate (**3p**).* Yield: 171.8 mg, (93 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.12 (s, 1H; Ar), 7.91-7.96 (m, 4H; Ar), 7.76-7.80 (m, 3H; Ar), 7.47-7.58 (m, 8H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 151.1 (d, ^{1}J (C,P) = 8.2 Hz; Ar), 135.5 (s; Ar), 133.8 (s; Ar), 132.8 (d, ^{1}J (C,P) = 2.8 Hz; Ar), 131.7 (d, ^{1}J (C,P) = 10.4 Hz; Ar), 130.5 (d, ^{1}J (C,P) = 137.2 Hz; Ar-C-P), 137.5 (s; Ar), 129.4 (s; Ar), 128.9 (s; Ar), 128.8 (d, ^{1}J (C,P) = 13.5 Hz; Ar), 127.1 (s; Ar), 122.6 (d, ^{1}J (C,P) = 5.1 Hz; Ar), 119.1 (s; CN), 117.3 (d, ^{1}J (C,P) = 5.1 Hz; Ar), 108.7 (s; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 31.84. HRMS calcd. for $C_{23}H_{16}NO_2P$: 369.0919, found: 369.0917.

*4.2.17. 2-Methyl-O-phenyl phenyl (phenyl) phosphinate (**3q**).* Yield: 100.4 mg, (65 %). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.86-7.91 (m, 4H; Ar), 7.45-7.54 (m, 6H; Ar), 7.24-7.26 (m, 1H; Ar), 7.13-7.14 (m, 1H; Ar), 6.96-7.03 (m, 2H; Ar), 2.30 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 149.6 (d, ^{1}J (C,P) = 8.3 Hz; Ar), 132.4 (d, ^{1}J (C,P) = 2.8 Hz; Ar), 131.7 (d, ^{1}J (C,P) = 10.4 Hz; Ar), 131.4 (d, ^{1}J (C,P) = 137.5 Hz; Ar-C-P), 131.3 (s; Ar), 129.1 (d, ^{1}J (C,P) = 5.7 Hz; Ar), 128.6 (d, ^{1}J (C,P) = 13.3 Hz; Ar), 126.9 (s; Ar), 124.4 (s; Ar), 120.2 (d, ^{1}J (C,P) = 3.7 Hz; Ar), 16.9 (s; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 29.91. HRMS calcd. for $C_{19}H_{17}O_2P$: 308.0966, found: 308.0964.

*4.2.18. 2,4-Di-methyl-O-phenyl phenyl (phenyl) phosphinate (**3r**).* Yield: 91.8 mg, (57 %). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.86-7.91 (m, 4H; Ar), 7.39-7.50 (m, 6H; Ar), 7.12-7.14 (m, 1H; Ar), 6.92 (s, 1H; Ar), 6.77-6.79 (m, 1H; Ar), 2.26 (s, 3H; CH_3), 2.17 (s, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 147.4 (d, ^{1}J (C,P) = 8.3 Hz; Ar), 133.8 (d, ^{1}J (C,P) = 0.8 Hz; Ar), 132.4 (d, ^{1}J (C,P) = 2.8 Hz; Ar), 131.9 (s; Ar), 131.7 (d, ^{1}J (C,P) = 10.3 Hz; Ar), 131.4 (d, ^{1}J (C,P) = 137.3 Hz; Ar-C-P), 128.7 (d, ^{1}J (C,P) = 5.6 Hz; Ar), 128.5 (d, ^{1}J (C,P) = 13.3 Hz; Ar), 127.3 (s; Ar), 119.9 (d, ^{1}J (C,P) = 3.5 Hz; Ar), 20.6 (s; Ar), 16.8 (s; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 29.72. HRMS calcd. for $C_{20}H_{19}O_2P$: 322.1123, found: 322.1120.

*4.2.19. Triphenyl phosphate (**4a**).*[12k] Yield: 171.8 mg, (93 %). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.44-7.37 (m, 6H; Ar), 7.19-7.25 (m, 9H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 150.5 (d, ^{1}J (C,P) = 7.4 Hz; Ar), 129.9 (s; Ar), 125.7 (s; Ar), 120.1 (d, ^{1}J (C,P) = 4.9 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= -17.66.

*4.2.20. Dibutyl phenyl phosphate (**4b**).*[12k] Yield: 104.6 mg, (73 %). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.14-7.45 (m, 5H; Ar), 4.12-4.17 (m, 4H; OCH_2), 1.65-1.69 (m, 4H; CH_2), 1.37-1.42 (m, 4H; CH_2), 0.92 (t, J = 7.2 Hz, 6H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 150.8 (d, ^{1}J (C,P) = 6.9 Hz; Ar), 129.6 (s; Ar), 124.9 (s; Ar), 119.9 (d, ^{1}J (C,P) = 4.8 Hz; Ar), 68.2 (d, ^{1}J (C,P) = 6.3 Hz; OCH_2), 32.2 (d, ^{1}J (C,P) = 6.8 Hz; CH_2), 18.6 (s; CH_2), 13.5 (s; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ = -6.11.

*4.2.21. Dibutyl O-phenyl phosphinate (**4c**).*[15f] Yield: 102.7 mg, (81 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.22-7.26 (m, 2H; Ar), 7.12-7.14 (m, 2H; Ar), 7.04-7.08 (m, 1H; Ar), 1.73-1.81 (m, 4H; CH_2), 1.52-1.58 (m, 4H; CH_2), 1.31-1.37 (m, 4H; CH_2), 0.84 (t, J = 7.2 Hz, 6H; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 58.35.

*4.2.22. Ethyl O-phenyl phenylphosphonate (**4d**).*[12k] Yield: 111.6 mg, (85 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.85-7.91 (m, 2H; Ar), 7.53-7.57 (m, 1H; Ar), 7.43-7.48 (m, 2H; Ar), 7.24-7.28 (m, 2H; Ar), 7.15-7.17 (m, 2H; Ar), 7.08-7.12 (m, 1H; Ar), 4.20-4.29 (m, 2H; OCH_2), 1.34 (t, J = 7.2 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 150.6 (d, ^{1}J (C,P) = 7.1 Hz; Ar), 132.8 (d, ^{1}J (C,P) = 3.1 Hz; Ar), 132.0 (d, ^{1}J (C,P) = 10.1 Hz; Ar), 129.6 (s; Ar), 128.5 (d, ^{1}J (C,P) = 15.3 Hz; Ar), 127.6 (d, ^{1}J (C,P) = 189.7 Hz; Ar-C-P), 124.8 (d, ^{1}J (C,P) = 1.0 Hz; Ar), 120.5 (d, ^{1}J (C,P) = 4.5 Hz; Ar), 62.9 (d, ^{1}J (C,P) = 5.9 Hz; OCH_2), 16.3 (d, ^{1}J (C,P) = 6.4 Hz; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 15.48.

*4.2.23. O-phenyl 4-methylphenyl (4-methylphenyl) phosphinate (**4e**).*[12k] Yield: 150.1 mg, (93 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.66-7.71 (m, 4H; Ar), 7.10-7.18 (m, 8H; Ar), 6.95-6.99 (m, 1H; Ar), 2.29 (s, 6H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 150.0 (d, J (C,P) = 8.1 Hz; Ar), 141.9 (d, J (C,P) = 2.9 Hz; Ar), 130.7 (d, J (C,P) = 10.7 Hz; Ar), 128.5 (s; Ar), 128.2 (d, J (C,P) = 13.7 Hz; Ar), 127.0 (d, J (C,P) = 140.0 Hz; Ar-C-P), 123.4 (s; Ar), 119.7 (d, J (C,P) = 4.8 Hz; Ar), 20.6 (s; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 31.41.

*4.2.24. O-phenyl 4-trifluoromethylphenyl (4-trifluoromethyl phenyl) phosphinate (**4f**).*[12k] Yield: 206.8 mg, (96 %). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.01-8.07 (m, 4H; Ar), 7.74-7.76 (m, 4H; Ar), 7.11-7.30 (m, 5H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 150.3 (d, ^{1}J (C,P) = 8.2 Hz; Ar), 134.6 (dd, ^{1}J (C,P) = 3.1 Hz, ^{2}J (C,F) = 32.8 Hz; Ar), 134.5 (d, ^{1}J (C,P) = 137.7 Hz; Ar-C-P), 132.3 (d, ^{1}J (C,P) = 10.6 Hz; Ar), 130.0 (s; Ar), 125.7 (dd, ^{1}J (C,P) = 3.7 Hz, ^{2}J (C,F) = 13.7 Hz; Ar), 125.3 (s; Ar), 123.4 (d, ^{2}J (C,F) = 272.0 Hz; -CF_3), 120.5 (d, ^{1}J (C,P) = 4.8 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 26.21; ^{19}F NMR (377 MHz, $CDCl_3$, 25 ^{o}C): δ= -63.4.

*4.2.25. O-phenyl-dibenzooxaphosphorine oxides (**4g**).*[12k] Yield: 144.5 mg, (94 %). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.93-8.03 (m, 3H; Ar), 7.70-7.74 (m, 1H; Ar), 7.47-7.52 (m, 1H; Ar), 7.36-7.40 (m, 1H; Ar), 7.20-7.29 (m, 4H; Ar), 7.09-7.13 (m, 1H; Ar), 7.03-7.05 (m, 2H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 149.9 (d, ^{1}J (C,P) = 8.2 Hz; Ar), 149.8 (d, ^{1}J (C,P) = 8.5 Hz; Ar), 137.1 (d, ^{1}J (C,P) = 7.0 Hz; Ar), 133.9 (d, ^{1}J (C,P) = 2.4 Hz; Ar), 130.7 (s; Ar), 129.7 (d, ^{1}J (C,P) = 0.9 Hz; Ar), 129.6 (d, ^{1}J (C,P) = 234.3 Hz; Ar-C-P), 128.3 (s; Ar), 125.3 (d, ^{1}J (C,P) = 1.5 Hz; Ar), 125.0 (s; Ar), 124.1 (d, ^{1}J (C,P) = 12.3 Hz; Ar), 122.6 (s; Ar), 122.5 (s; Ar), 120.7 (s; Ar), 120.6 (s; Ar), 120.3 (d, ^{1}J (C,P) = 6.9 Hz; Ar); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 6.48.

*4.2.26. 1,2-Bis(4-tert-butylphenyl)disulfane (**5**).*[15g] Yield: 145.3 mg, (88 %). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.31-7.45 (m, 8H; Ar), 1.29 (s, 18H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 150.5 (s; Ar), 134.1 (s; Ar), 127.8 (s; Ar), 126.1 (s; Ar), 34.6 (s; -$C(CH_3)_3$), 31.3 (s; CH_3).

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Supplementary Material

Supplementary data associated with this article can be found in the online version.

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