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Note

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Bu_4NI Catalyzed Dehydrogenative Coupling of Diaryl Phosphinic Acids with Csp^3-H Bonds of Arenes

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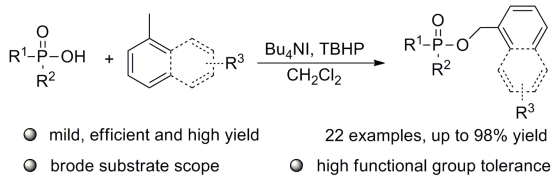
Abstract

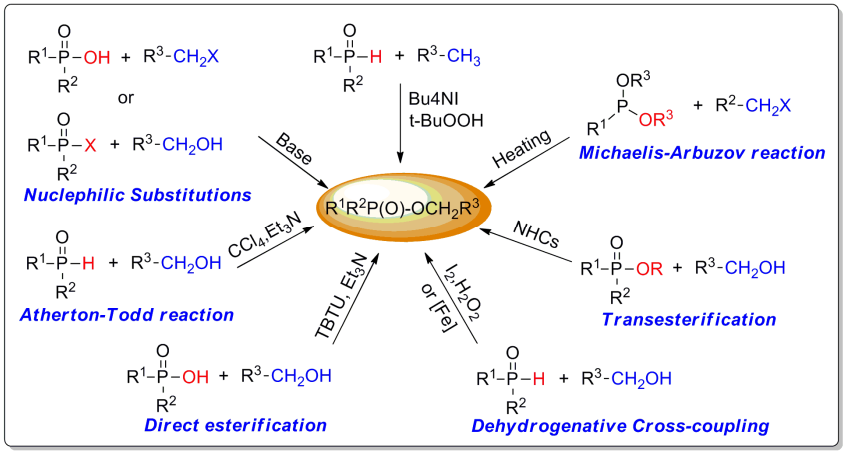


An efficient phosphorylation of Csp^3-H bonds of arenes with diaryl phosphinic acids via Bu_4NI catalyzed dehydrogenative coupling has been developed. This transformation proceeds efficiently under transition metal-free reaction conditions, and represents a straightforward method to prepare valuable organophosphorus compounds from the readily available arenes and diaryl phosphinic acids.

As fundamental starting materials, organophosphorus compounds are versatile substrates in organic transformations. Especially some phosphate esters are very useful in functional materials and industrial science (*e.g.*,tris(2-ethylhexyl) phosphate is used as a plasticizer for vinyl polymers and triaryl phosphates are also manufactured commercially and used as additives for gasoline, polymer

plasticizers.).[1-3] Phosphoric acid esters are of great commercial importance, and a valuable summary has been prepared by Toy and Walsh.[4] The increasing interest of these compounds is mainly related to the wide presence of the phosphonic functionality (acid or ester) in many natural or synthetic bioactive compounds. Nonetheless, they are costly due to rare availability from nature. As depicted in Scheme 1, the most straightforward method of preparing such compounds is the straightforward transformation pathway between a P(O)-H/P(O)-X compounds and a nucleophiles, apart from the conventional nucleophilic substitution protocols.

Scheme 1 Traditional methods for the synthesis of phosphonate/phosphate esters.



The direct phosphorylation of nucleophiles is extensively used for the synthesis of organophosphorus compounds, but these approaches suffer from the low tolerance of functional groups and substrate limitations (*e.g.*, Atherton-Todd reaction, nucleophilic substitutions).[5a] In 2013, Prabhu *et al.* reported a green, direct cross-coupling of phosphites with alcohols in the presence of I_2/H_2O_2 at room temperature.[5b] In 2016, Chen and Han *et al.* further reported an efficient procedure based on iron-catalyzed dehydrogenative coupling of P(O)-H compounds with alcohols, using $Fe(AcAc)_2$ as iron source and toluene as solvent, under N_2 atmosphere.[5c] Nolan *et al.* disclosed the direct synthesis of phosphorus esters by transesterification mediated by *N*-heterocyclic carbenes in 2005.[5d] Later, Tang and Zhao *et al.* investigated the phosphorylation of benzyl C-H bonds via a cross-dehydrogenative coupling

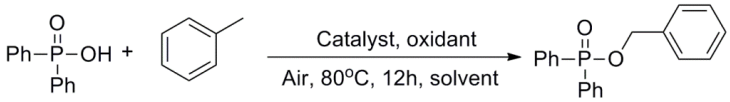
path of using P(O)-H compounds as the starting materials.[5e] Although there are a large number of studies on the phosphorylation of nucleophiles, the use of P(O)-OH compounds as starting materials is rare. Indeed, literatures about the metal-catalyzed cross-coupling reaction of P(O)-OH compounds with Csp^3-H bonds of arenes have not been reported. Thus, to develop an efficient and convenient method for the selective functionalization of P(O)-OH compounds is highly desired in organophosphorus chemistry.

To avoid the prefunctionalization of reactants, the direct dehydrogenative coupling of Csp^3-H bonds of arenes with organophosphorus compounds containing a P(O)-OH moiety under mild conditions will become an efficient and promising strategy for the formation of phosphinic and phosphoric esters.[6-7] Very rencently, we have reported the direct esterification of P(O)-OH compounds with alcohols or phenols under mild reaction conditions.[8] As an ongoing effort on the activation of P(O)-OH compounds, we herein report an efficient and simple oxidative dehydrogenative coupling of P(O)-OH compounds with Csp^3-H bonds of arenes under mild conditions using a cheap quaternary ammonium salt catalyst. 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.[9-11]

The reaction of diphenyl phosphinic acid (**1a**) with toluene (**2a**) with the addition of TBHP (*tert*-butyl hydroperoxide, 2.0 equivalent), Bu_4NI (tetrabutylammonium iodide, 10 mol%) and 1.0 mL of toluene under air gave the desired product of benzyl diphenyl phosphonate (**3a**) in 67% yield. In the reaction, toluene was in excess and served as solvent. Then we concentrated on the optimization of reaction conditions. At the initial, we screened several catalysts for the reaction, and found that Bu_4NI was the best. To our surprise, Bu_4NBr, 18-crown-6-ether and I_2 showed negative to the reaction (Table 1, entries1-4). Different oxidants such as $K_2S_2O_8$, TBPB (*tert*-butyl peroxybenzoate), TBHP (*tert*-butyl hydroperoxide), H_2O_2, *m*-CPBA (3-chloroperoxybenzoic), $H_3K_5O_{18}S_4$ and DTPB (*di*-*tert*-butyl peroxide) were further tested for the reaction. It was worth noting that the organic oxidants were much more effective than the inorganic oxidants. This phenomenon may be ascribe to the reaction of inorganic bases with P(O)-OH compounds to form the corresponding salts in the reaction, which inhibited the cross-coupling process (Table 1, entries 5-10). With the addition of TBHP increased to 3.0 equivalents,

the yield of **3a** was increased from 67% to 76%. Further increasing the addition of TBHP did not result in the raise for the yield of **3a** significantly, so we adopted the 3.0 equivalents of TBHP as the oxidant for the reaction. The catalyst loading also affected the reaction obviously. With the amount of Bu_4NI increased from 20 mol% to 30 mol%, the expected coupling product of **3a** was gained in 83% and 85% yields, so we chose 20 mol% of Bu_4NI as the best catalyst loading (Table 1, entries 11-14). When the reaction was operated in 60 ^oC, it was only 47% yield of **3a** generated after the reaction. Further increasing the temperature from 80 ^oC to 100 ^oC, the yield of **3a** was decreased from 83% to 61%. In order to expand the applications of the reaction, different solvents were investigated (CH_2Cl_2, Dioxane, DMF, $ClCH_2CH_2Cl$, CH_3CN, CH_3OH, THF), and CH_2Cl_2 was found to be the best, affording **3a** in 98% yield (Table 1, entries 17-23). Therefore, the optimal reaction conditions are as follows: diphenyl phosphinic acid (0.5 mmol), toluene (0.5 mmol), TBHP (1.5 mmol), Bu_4NI (20 mol%), CH_2Cl_2 (0.5 mL), 80 ^oC, 12 h.

Table1 Optimization of the reaction conditions [a].



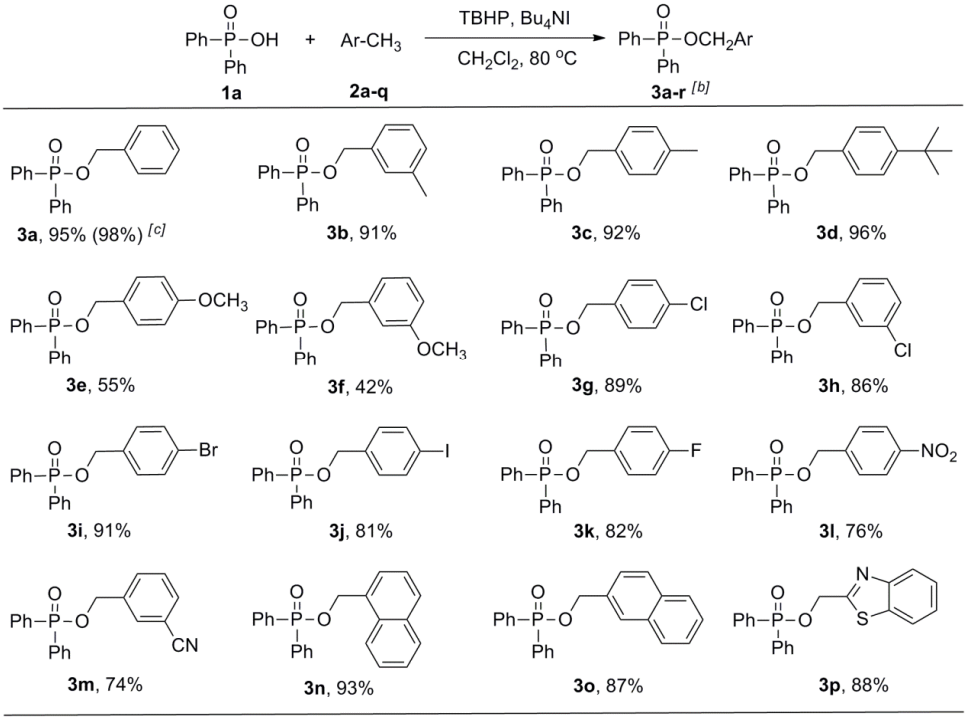
1a **2a** **3a**

Entry	Cat. (mol%)	Oxidant (equiv)	Solvent	Yield [b]
1	Bu_4NI (10)	TBHP (2.0)	Toluene	67%
2	Bu_4NBr (10)	TBHP (2.0)	Toluene	0%
3	18-crown-6-ether (10)	TBHP (2.0)	Toluene	0%
4	I_2 (10)	TBHP (2.0)	Toluene	0%
5	Bu_4NI (10)	$K_2S_2O_8$ (2.0)	Toluene	26%
6	Bu_4NI (10)	TBPB (2.0)	Toluene	36%
7	Bu_4NI (10)	H_2O_2 (2.0)	Toluene	trace
8	Bu_4NI (10)	*m*-CPBA (2.0)	Toluene	trace
9	Bu_4NI (10)	$H_3K_5O_{18}S_4$ (2.0)	Toluene	0%
10	Bu_4NI (10)	DTBP (2.0)	Toluene	0%
11	Bu_4NI (10)	TBHP (3.0)	Toluene	76%
12	Bu_4NI (10)	TBHP (4.0)	Toluene	78%
13	Bu_4NI (20)	TBHP (3.0)	Toluene	83%
14	Bu_4NI (30)	TBHP (3.0)	Toluene	85%
15	Bu_4NI (20)	TBHP (3.0)	Toluene	47% [c]
16	Bu_4NI (20)	TBHP (3.0)	Toluene	61% [d]
17	Bu_4NI (20)	TBHP (3.0)	CH_2Cl_2	98%

18	Bu_4NI (20)	TBHP (3.0)	Dioxane	0%
19	Bu_4NI (20)	TBHP (3.0)	DMF	0%
20	Bu_4NI (20)	TBHP (3.0)	DCE	<10%
21	Bu_4NI (20)	TBHP (3.0)	CH_3CN	trace
22	Bu_4NI (20)	TBHP (3.0)	CH_3OH	<5%
23	Bu_4NI (20)	TBHP (3.0)	THF	trace

[a] Diphenyl phosphinic acid (0.5 mmol), toluene (1.0 mL for entries 1-16, 0.5 mmol for entries 17-23), catalyst, and oxidant, solvent (0.5 mL), air, 80 °C, 12h. [b] Yield was determined by GC analysis, and decane was used as the internal standard. [c] 60 °C. [d] 100 °C.

Table 2 Scope of methyl substituted arenes [a].

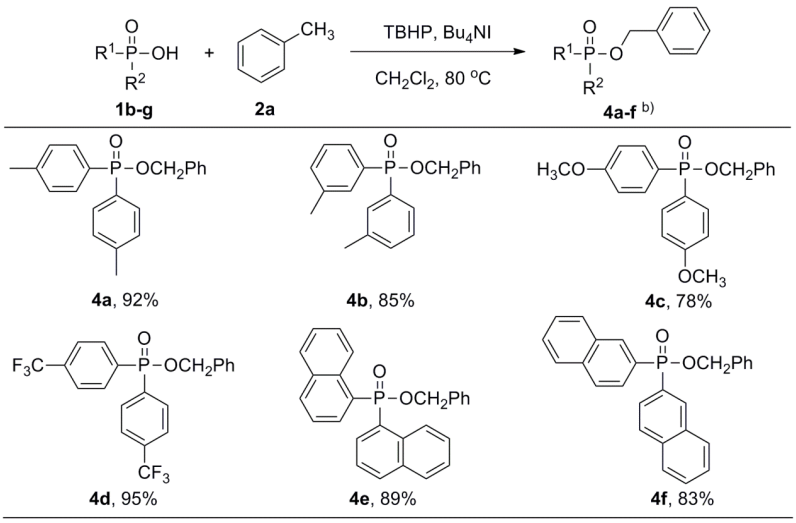


[a] Reaction conditions: $Ph_2P(O)OH$ (0.5 mmol), arenes (0.5mmol), TBHP (1.5 mmol), Bu_4NI (0.1 mmol), CH_2Cl_2 (0.5 mL), air, 80 °C, 12 h. [b] Isolated yields. [c] GC yield, decane was used as the internal standard.

As shown in Table 2, the present esterification reaction can be applied to a variety of methyl substituted arenes. It is clear that *m*-xylene, *p*-xylene and 1-*tert*-butyl-4-methyl benzene can react efficiently with diphenyl phosphinic acid (**1a**) under the optimized reaction conditions, affording the corresponding coupling products of **3b-3d** in 91-96% yields. Electron-donating group substituted arenes such as 1-methoxy-4-methyl benzene and 1-methoxy-3-methyl benzene only gave the desired products

of **3e** and **3f** in 55% and 42% yields. It was worth noting that the electron-withdrawing groups substituted arenes such as 1-chloro-4-methylbenzene, 1-chloro-3-methylbenzene, 1-bromo-4-methylbenzene, 1-iodo-4-methylbenzene, 1-fluoro-4-methylbenzene, 1-nitro-4-methylbenzene and 3-methylbenzonitrile were also well tolerated on the reaction, producing the corresponding coupling products of **3g-3m** in 74-91% yields. Interestingly, 1-methylnaphthalene and 2-methylnaphthalene both showed high activities toward the reaction, yielding the expected products of naphthalen-1-ylmethyl diphenylphosphinate (**3n**) and naphthalen-2-ylmethyl diphenylphosphinate (**3o**) in 93% and 87% yields. Moreover, heterocyclic organophosphorus compounds such as benzo[*d*]thiazol-2-ylmethyl diphenylphosphinate (**3p**) could also be synthesized from diphenyl phosphinic acid and 2-methylbenzo[*d*]thiazole in 88% yield via the Bu_4NI catalyzed dehydrogenative coupling reaction.

Table 3 Scope of P(O)OH compound [a)].

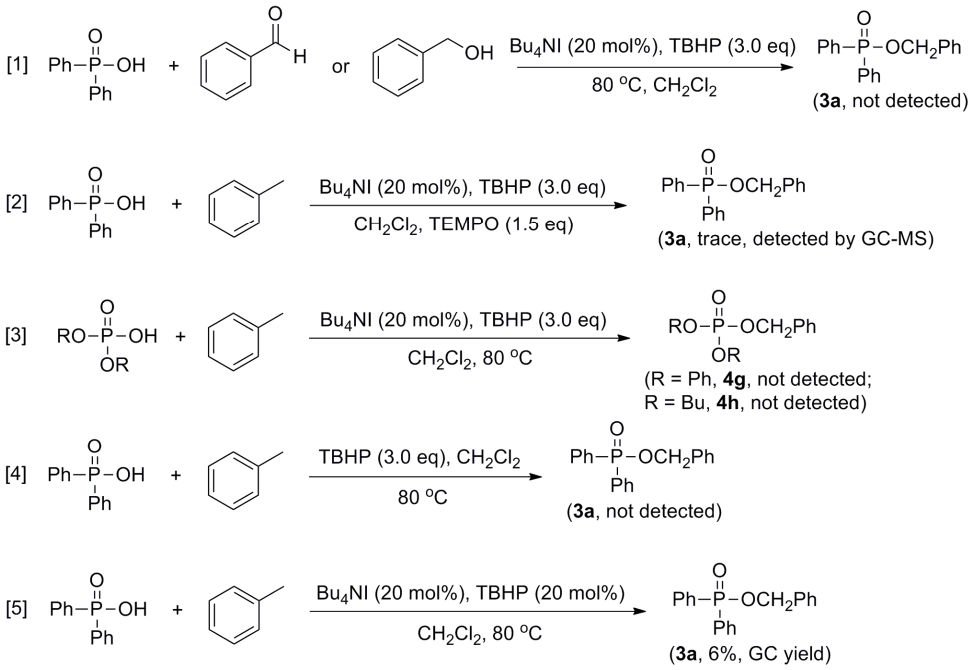


[a] Reaction conditions: diaryl phosphinic acids (0.5 mmol), toluene (0.5 mmol), TBHP (1.5 mmol), Bu_4NI (0.1 mmol), CH_2Cl_2 (0.5 mL), air, 80 °C, 12 h. [b] Isolated yield.

As depicted in Table 3, different substituted diaryl phosphinic acids such as *di*-(4-methyl phenyl) phosphinic acid, *di*-(3-methyl phenyl) phosphinic acid, *di*-(4-methoxyphenyl) phosphinic acid, *di*-(4-trifluoromethylphenyl) phosphinic acid and *di*-(1-methylnaphthalene) phosphinic acid (**4c**) could react efficiently with toluene under the optimized reaction conditions, affording the expected coupling

products of **4a-4d** in 78-95% yields. To our delight, *di*-(1-methylnaphthalene) phosphinic acid and *di*-(2-methylnaphthalene) phosphinic acid also showed positive to the reaction, and the corresponding coupling phosphinic esters of benzyl di(naphthalen-1-yl)phosphinate (**4e**) and benzyl di(naphthalen-2-yl)phosphinate (**4f**) were generated in 89% and 83% yields, respectively.

Scheme2 Control experiments.

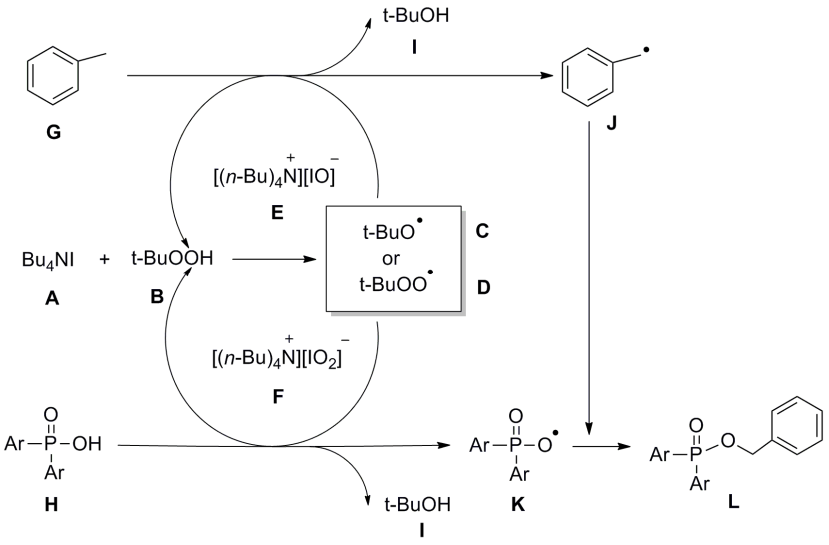


In order to clarify the reaction mechanism, we operated the reaction of diphenyl phosphinic acid with benzaldehyde or phenylmethanol in the presence of Bu_4NI and TBHP under the optimized reaction conditions. At the beginning of this study, benzyl alcohol or benzyl aldehyde was assumed to be a potential intermediate in the reaction. As confirmed by GC, GC-MS, and ^{31}P NMR analysis, there was no detection of the coupling product (Scheme 2, path 1). When the radical scavenger 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO) was added in the reaction, only a trace amount of **3a** was observed. It is hence deduced that the reaction possibly occurs through an oxidative dehydrogenative coupling path rather than the esterification path. When diphenyl hydrogen phosphate or dibutyl hydrogen phosphate was used to the reaction, the corresponding dehydrogenative coupling products of benzyl diphenyl phosphate (**4g**) or benzyl dibutyl phosphate (**4h**) could not be detected after the reaction.

This phenomenon may be ascribed to the strong acidity of this type of compounds. If the reaction operated without the use of catalyst, the reaction could not proceed as we expected. In addition, the catalytic amount of TBHP (20 mol%) could only give **3a** in 6% yield under the optimized conditions.

A plausible catalytic cycle is presented in scheme 3. Bu_4NI (**A**) first attacks *tert*-butyl hydroperoxide (**B**) to afford the intermediate radicals of **C** and **D** or the corresponding adducts of **E** and **F**. Then these intermediates take the hydrogen atom from arenes (**G**) and diaryl phosphinic acids (**H**) to generate the benzyl radical **J** and phosphoryl radical **K**. Meanwhile, one molecule of *tert*-butyl alcohol (**I**) is generated. Finally, the oxidative dehydrogenation coupling path is completed via the reaction of activated intermediate radicals of **J** and **K** to yield the desired phosphinates (**L**).

Scheme3. Proposed reaction mechanism.



Conclusions

In summary, we develop an efficient method for the preparation of phosphinates via Bu_4NI catalyzed oxidative dehydrogenation coupling of diary phosphinic acids with methyl substituted arenes. Both diary phosphinic acids and methyl substituted arenes are commercially available and easily synthesized. The method avoids the use of moisture/air-sensitive substrates and metal catalysts. Moreover, the method is

tolerant of many substrates, operationally simple, and can be performed under ambient conditions. The above superiority of this method renders it a powerful complement to traditional approaches for the synthesis of phosphinic acid esters.

Experimental Section

General Considerations:

All solvents used in the reactions were freshly distilled. The other reagents were recrystallized or distilled as necessary. All reactions were performed under air atmosphere unless specified otherwise. ^{1}H (400 MHz), ^{13}C (100 MHz) spectra were recorded on a 400MHz spectrometer with the sample dissolved in $CDCl_3$. ^{1}H NMR chemical shifts were reported using TMS as internal standard while ^{13}C NMR chemical shifts were reported relative to $CDCl_3$. The electron ionization method was used for HRMS measurements, and the mass analyzer type was double-focusing.

General procedure:

A mixture of P(O)-OH compounds (0.5 mmol), arenes (0.5 mmol), Bu_4NI (0.1 mmol) and TBHP (1.5 mmol) was dissolved in CH_2Cl_2 under air atmosphere, stirred at 80 ^{o}C for 12h. Removal of the solvent under a reduced pressure gave the crude product; pure product was obtained by passing the crude product through a short silica gel column using Hexane/EtOAc (1:1-5:1) as eluent.

O-benzyl diphenylphosphinate (3a): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3a** (146.0 mg, 0.474 mmol, 95 %) as a yellow oil.[11a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.72-7.77 (m, 4H), 7.40-7.44 (m, 2H), 7.34-7.37 (m, 4H), 7.17-7.27 (m, 5H), 4.98 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 136.3 (d, ^{1}J (C,P) = 7.6 Hz), 132.3 (d, ^{1}J (C,P) = 2.8 Hz), 131.7 (d, ^{1}J (C,P) = 10.2 Hz), 131.3 (d, ^{1}J (C,P) = 136.0 Hz), 128.7 (s), 128.6 (d, ^{1}J (C,P) = 4.0 Hz), 128.3 (s), 127.9 (s), 66.4 (d, ^{1}J (C,P) = 5.6 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.46.

O-3-methylbenzyl diphenylphosphinate (3b): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 1:1) gave product **3b** (146.5 mg, 0.455 mmol, 91 %) as a

yellow oil.[5c] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.81-7.86 (m, 4H), 7.44-7.51 (m, 6H), 7.21-7.25 (m, 1H), 7.11-7.17 (m, 3H), 5.02-5.03 (d, *J* = 6.4 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 138.2 (s), 136.2 (d, ^1J (C,P) = 7.4 Hz), 132.2 (d, ^1J (C,P) = 2.8 Hz), 131.8 (d, ^1J (C,P) = 10.1 Hz), 131.4 (d, ^1J (C,P) = 135.0 Hz), 129.1 (s), 128.7 (s), 128.6 (s), 128.5 (s), 125.0 (s), 66.4 (d, ^1J (C,P) = 5.5 Hz), 21.4 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.31.

O-4-methylbenzyl diphenylphosphinate (3c): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3c** (148.1 mg, 0.46 mmol, 92 %) as a yellow oil.[11a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.80-7.85 (m, 4H), 7.50-7.53 (m, 2H), 7.42-7.46 (m, 4H), 7.24-7.26 (m, 2H), 7.14-7.16 (m, 2H), 5.02 (d, *J* = 6.8, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 138.2 (s), 132.2 (d, ^1J = 2.8 Hz), 131.7 (d, ^1J = 10.2 Hz), 131.4 (d, ^1J (C,P) = 135.9 Hz), 129.2 (s), 128.6 (s), 128.5 (s), 128.1 (s), 66.3 (d, ^1J (C,P) = 5.6 Hz), 21.2 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.2.

O-4-(tert-butyl)benzyl diphenylphosphinate (3d): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3d** (174.9 mg, 0.48 mmol, 96 %) as a yellow oil.[11b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.81-7.85 (m, 4H), 7.49-7.53 (m, 2H), 7.42-7.45 (m, 4H), 7.36-7.37 (m, 2H), 7.29-7.31 (m, 2H), 5.04 (d, *J* = 6.4Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 151.4 (s), 133.3 (d, ^1J (C,P) = 7.4 Hz), 132.2 (d, ^1J (C,P) = 2.7 Hz), 131.8 (d, ^1J (C,P) = 10.1 Hz), 131.4 (d, ^1J (C,P) = 135.9 Hz), 128.6 (d, ^1J (C,P) = 13.1 Hz), 127.8 (s), 125.5 (s), 66.2 (d, ^1J = 5.4 Hz), 34.6 (s), 31.3 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.2.

O-4-methoxybenzyl diphenylphosphinate (3e): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3e** (87.9 mg, 0.26 mmol, 52 %) as colorless oil.[8b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.71-7.76 (m, 4H), 7.39-7.43 (m, 2H), 7.31-7.35 (m, 4H), 7.13-7.17 (m, 1H), 6.73-6.85 (m, 3H), 4.94 (d, *J* = 6.8 Hz, 2H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 159.7 (s), 137.8 (d, ^1J (C,P) = 7.4 Hz), 132.3 (d, ^1J (C,P) = 2.8 Hz), 131.7 (d, ^1J (C,P) = 10.2 Hz), 131.3 (d, ^1J (C,P) = 135.9 Hz), 128.6 (d, ^1J (C,P) = 13.1 Hz),

120.1 (s), 113.6 (d, ^1J (C,P) = 7.4 Hz), 66.2 (d, ^1J (C,P) = 5.5 Hz), 55.2 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.5.

O-3-methoxybenzyl diphenylphosphinate (3f): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 1:1) gave product **3e** (70.9 mg, 0.21 mmol, 42 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.73-7.78 (m, 4H), 7.37-7.45 (m, 6H), 7.16-7.20 (m, 1H), 6.83-6.87 (m, 2H), 6.77-6.79 (m, 1H), 4.97 (d, J = 6.4 Hz, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 159.7 (s), 132.3(d, ^1J (C,P) = 2.6Hz), 131.7 (d, ^1J (C,P) = 10.2 Hz), 131.3 (d, ^1J (C,P) = 136.0 Hz), 129.6 (s), 128.7 (s), 128.5 (s), 120.1 (s), 113.9 (s), 113.3 (s), 66.2 (d, ^1J (C,P) = 5.5 Hz), 55.3 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.5. HRMS (EI) m/z: calcd. for $C_{20}H_{19}O_3P$: 338.1072, found: 338.1069.

O-4-chlorobenzyl diphenylphosphinate (3g): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3g** (152.2 mg, 0.445 mmol, 89 %) as a yellow oil.[5c] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.79-7.84 (m, 4H), 7.45-7.53 (m, 6H), 7.30-7.34 (m, 4H), 5.03 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 134.9 (d, ^1J (C,P) = 7.0 Hz), 134.2 (s), 132.4 (d, ^1J (C,P) = 2.7 Hz), 131.7 (d, ^1J (C,P) = 10.2 Hz), 131.1 (d, ^1J (C,P) = 136.1 Hz), 129.3 (s), 128.7 (d, ^1J (C,P) = 5.7 Hz), 128.6 (s), 65.6 (d, ^1J (C,P) = 5.5 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.8.

O-3-chlorobenzyl diphenylphosphinate (3h): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 1:1) gave product **3h** (147.1 mg, 0.43 mmol, 86 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.81-7.86 (m, 4H), 7.46-7.54 (m, 6H), 7.25-7.34 (m, 4H), 5.04 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 138.3 (d, ^1J (C,P) = 7.8 Hz), 134.4 (s), 132.4 (d, ^1J (C,P) = 2.6 Hz), 131.7 (d, ^1J (C,P) = 10.3 Hz), 130.3 (s), 129.2 (d, ^1J (C,P) = 142.8 Hz), 128.7 (d, ^1J (C,P) = 13.1 Hz), 127.9 (s), 125.9 (s), 100.0(s), 65.5 (d, ^1J (C,P) = 5.5 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 33.0. HRMS (EI) m/z: calcd. for $C_{19}H_{16}ClO_2P$: 342.0576, found: 342.0574.

O-4-bromobenzyl diphenylphosphinate (3i): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3i** (175.6 mg, 0.455 mmol, 91 %) as a yellow oil.[8b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.79-7.84 (m, 4H), 7.51-7.55 (m, 2H), 7.45-7.47 (m, 6H), 7.22-7.26 (m, 2H), 5.01 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 135.4 (d, ^{1}J (C,P) = 7.0 Hz), 132.4 (d, ^{1}J (C,P) = 2.8 Hz), 131.7 (d, ^{1}J (C,P) = 1.2 Hz), 131.6 (s), 131.0 (d, ^{1}J (C,P) = 117.8 Hz), 129.6 (s), 128.6 (d, ^{1}J (C,P) = 13.2 Hz), 122.4 (s), 65.6 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.9.

O-4-iodobenzyl diphenylphosphinate (3j): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3i** (175.4 mg, 0.405 mmol, 81 %) as a yellow oil.[5e] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.79-7.84 (m, 4H), 7.66-7.68 (m, 2H), 7.45-7.55 (m, 6H), 7.09-7.11 (m, 2H), 5.00 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 137.7 (s), 136.0 (s), 132.4 (d, ^{1}J (C,P) = 2.7 Hz), 131.7 (d, ^{1}J (C,P) = 10.3 Hz), 131.1 (d, ^{1}J (C,P) = 136.0 Hz), 129.7 (s), 128.6 (d, ^{1}J (C,P) = 13.1 Hz), 94.0 (s), 65.7 (d, ^{1}J (C,P) = 5.4 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.8.

O-4-fluoro-benzyl phenyl (phenyl) phosphinate (3k): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3k** (149.9 mg, 0.46mmol, 92 %) as a colorless oil.[11a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.80-7.86 (m, 4H), 7.48-7.52 (m, 2H), 7.41-7.45 (m, 4H), 7.31-7.35 (m, 2H), 6.99-7.03 (m, 2H), 5.03 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 162.6 (d, ^{1}J (C,F) = 245.5 Hz), 132.3 (d, ^{1}J (C,P) = 2.8 Hz), 132.2 (dd, ^{1}J (C,P) = 3.2 Hz, ^{2}J (C,F) = 3.1 Hz), 131.6 (d, ^{1}J (C,P) = 10.2 Hz), 131.2 (d, ^{1}J (C,P) = 135.9 Hz), 129.9 (d, ^{1}J (C,P) = 8.3 Hz), 128.5 (d, ^{1}J (C,P) = 13.2 Hz), 115.4 (d, ^{1}J (C,P) = 21.5 Hz), 65.6 (d, ^{1}J (C,P) = 5.4 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 33.6.

O-4-nitrobenzyl diphenylphosphinate (3l): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3l** (144.7 mg, 0.41 mmol, 82 %) as a yellow oil.[11a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.21 (d, *J* = 8.0 Hz, 2H), 7.81-7.86 (m, 4H), 7.48-7.58 (m, 8H), 5.16 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 147.8 (s),

143.6 (d, ^{1}J (C,P) = 7.0 Hz), 132.6 (d, ^{1}J (C,P) = 2.7 Hz), 131.6 (d, ^{1}J (C,P) = 10.3 Hz), 130.7 (d, ^{1}J (C,P) = 136.0 Hz), 128.7 (d, ^{1}J (C,P) = 13.2 Hz), 128.1 (s), 123.8 (s), 64.9 (d, ^{1}J (C,P) = 5.3 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 33.6.

O-3-cyanobenzyl diphenylphosphinate (3m): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 1:1) gave product **3m** (123.2 mg, 0.37 mmol, 74 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.80-7.85 (m, 4H), 7.54-7.64 (m, 5H), 7.44-7.50 (m, 5H), 5.10 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 138.0 (d, ^{1}J (C,P) = 7.3 Hz), 132.6 (d, ^{1}J (C,P) = 2.8 Hz), 131.9 (d, ^{1}J (C,P) = 9.6 Hz), 131.7 (d, ^{1}J (C,P) = 10.2 Hz), 131.1 (s), 130.8 (d, ^{1}J (C,P) = 135.8 Hz), 129.4 (s), 128.7 (d, ^{1}J (C,P) = 13.2 Hz), 118.5 (d, ^{1}J (C,P) = 2.7 Hz), 112.8 (s), 65.0 (d, ^{1}J (C,P) = 5.3 Hz), 13.8 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 33.4. HRMS (EI) m/z: calcd. for $C_{20}H_{16}NO_2P$: 333.0919, found: 333.0917.

O-naphthalen-1-ylmethyl diphenylphosphinate (3n): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3n** (166.5 mg, 0.465 mmol, 93 %) as a yellow oil.[11a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.09 (d, J = 8.0 Hz, 1H), 7.78-7.86 (m, 6H), 7.37-7.54 (m, 10H), 5.53 (d, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 133.7 (s), 132.3 (d, ^{1}J (C,P) = 2.7 Hz), 131.8 (d, ^{1}J (C,P) = 7.5 Hz), 131.7 (d, ^{1}J (C,P) = 10.2 Hz), 131.3 (d, ^{1}J (C,P) = 135.8 Hz), 129.4 (s), 128.7 (s), 128.6 (s), 128.5 (s), 127.0 (s), 126.6 (s), 126.0 (s), 125.2 (s), 123.7 (s), 66.8 (d, ^{1}J (C,P) = 5.5 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.6.

O-naphthalen-2-ylmethyl diphenylphosphinate (3o): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **3n** (155.7 mg, 0.435 mmol, 87 %) as a yellow oil.[5e] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.77-7.88 (m, 8H), 7.47-7.53 (m, 9H), 5.22 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 133.8 (d, ^{1}J (C,P) = 7.4 Hz), 133.2 (d, ^{1}J (C,P) = 2.1 Hz), 132.3 (d, ^{1}J (C,P) = 2.7 Hz), 131.8 (s), 131.7 (s), 131.3 (d, ^{1}J (C,P) = 135.8 Hz), 128.7 (s), 128.5 (s), 128.4 (s), 128.0 (s), 127.7 (s), 127.1 (s), 126.3 (s), 125.7 (s), 66.6 (d, ^{1}J (C,P) = 5.5 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.5.

O-benzo[d]thiazol-2-ylmethyl diphenylphosphinate (3p): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 5:1) gave product **3n** (160.6 mg, 0.44 mmol, 88 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.00 (d, *J* = 8.0 Hz, 1H), 7.87-7.92 (m, 5H), 7.39-7.52 (m, 8H), 5.43 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 135.1 (s), 134.9 (s), 132.7 (d, ^{1}J (C,P) = 2.7 Hz), 132.0 (d, ^{1}J (C,P) = 192.1 Hz), 131.8 (d, ^{1}J (C,P) = 10.4 Hz), 128.8 (d, *J* = 13.2 Hz), 126.3 (s), 125.4 (s), 123.3 (s), 121.8 (s), 108.2 (d, ^{1}J (C,P) = 6.7 Hz), 63.6 (d, ^{1}J (C,P) = 4.6 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 34.1. HRMS (EI) m/z: calcd. for $C_{20}H_{16}NO_2PS$: 365.0639, found: 365.0635.

O-benzyl di-p-tolylphosphinate (4a): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **4a** (154.6 mg, 0.46 mmol, 92 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.69-7.74 (m, 4H), 7.32-7.35 (m, 5H), 7.24-7.26 (m, 4H), 5.04 (d, *J* = 6.4 Hz, 2H), 2.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 142.7(d, ^{1}J (C,P) = 2.9 Hz), 131.7 (d, ^{1}J (C,P) = 10.6 Hz), 129.4 (d, ^{1}J (C,P) = 118.9 Hz), 129.3 (d, ^{1}J (C,P) = 13.5 Hz), 128.5 (s), 128.2 (s), 127.8 (s), 127.4 (s), 66.2 (d, ^{1}J (C,P) = 5.4 Hz), 21.6 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 33.6. HRMS (EI) m/z: calcd. for $C_{21}H_{21}O_2P$: 336.1279, found: 336.1277.

O-benzyl di-m-tolylphosphinate (4b): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **4b** (142.8 mg, 0.425 mmol, 85 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.58-7.67 (m, 4H), 7.26-7.36 (m, 9H), 5.05 (d, *J* = 6.8 Hz, 2H), 2.35 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 138.5 (s), 138.4 (s), 133.1 (d, ^{1}J (C,P) = 2.9 Hz), 132.2 (d, ^{1}J (C,P) = 10.3 Hz), 131.2 (d, ^{1}J (C,P) = 135.2 Hz), 128.8 (d, ^{1}J (C,P) = 10.0 Hz), 128.5 (s), 128.3 (d, ^{1}J (C,P) = 14.9 Hz), 127.9 (s), 100 (s), 66.3 (d, ^{1}J (C,P) = 5.5 Hz), 21.4 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 33.2. HRMS (EI) m/z: calcd. for $C_{21}H_{21}O_2P$: 336.1279, found: 336.1275.

O-benzyl bis(4-methoxyphenyl)phosphinate (4c): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **4c** (143.5 mg, 0.39 mmol, 78 %) as a yellow oil.[5e] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.64-7.69 (m, 4H), 7.24-7.27 (m, 5H), 6.85-6.87 (m, 4H), 4.94 (d, *J* = 6.4 Hz, 2H), 3.74 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ=

162.6 (d, ^{1}J (C,P) = 3.0 Hz), 136.7 (d, ^{1}J (C,P) = 7.9 Hz), 133.6 (d, ^{1}J (C,P) = 11.5 Hz), 128.5 (s), 128.2 (s), 127.8 (s), 122.9 (d, ^{1}J (C,P) = 143.5 Hz), 114.1 (d, J = 14.1 Hz), 66.0 (d, J = 5.3 Hz), 55.3 (s); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 33.3.

O-benzyl bis(4-(trifluoromethyl)phenyl)phosphinate (4d): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **4d** (210.9 mg, 0.475 mmol, 95 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 7.92-7.97 (m, 4H), 7.70-7.72 (m, 4H), 7.27-7.35 (m, 5H), 5.12 (d, J = 7.6Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 135.0 (d, ^{1}J (C,P) = 135.2 Hz), 135.5 (d, ^{1}J (C,P) = 6.7 Hz), 132.2 (d, ^{1}J (C,P) = 10.5 Hz), 128.8 (s), 128.7 (s), 128.2 (s), 125.6 (dd,^{1}J (C,P) = 9.7 Hz, ^{2}J (C,F) = 17.1 Hz), 124.7 (s), 122.1 (s), 66.2 (d, ^{1}J (C,P) = 5.2 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 28.4. HRMS (EI) m/z: calcd. for $C_{21}H_{15}F_6O_2P$: 444.0714, found: 444.0711.

O-benzyl di(naphthalen-1-yl)phosphinate (4e): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **4e** (181.2 mg, 0.445 mmol, 89 %) as a colorless oil.[7d] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.6 (d, J = 8.0 Hz, 2H), 8.16-8.21 (m, 2H), 8.05 (d, J = 8.2 Hz, 2H), 7.86 (d, J = 6.8 Hz, 2H), 7.40-7.52 (m, 6H), 7.24-7.34 (m, 5H), 5.15-5.17 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 138.2 (d, ^{1}J (C,P) = 8.0 Hz), 134.2 (d, ^{1}J (C,P) = 10.1 Hz), 133.7 (d, ^{1}J (C,P) = 3.0 Hz), 132.7 (s), 132.0 (d, ^{1}J (C,P) = 10.1 Hz), 130.0 (s), 128.9 (d, ^{1}J (C,P) = 1.3 Hz), 128.5 (s), 128.2 (d, ^{1}J (C,P) = 3.4 Hz), 127.5 (s), 127.6 (d, ^{1}J (C,P) = 138.0 Hz), 126.6 (d, ^{1}J (C,P) = 4.9 Hz), 126.4 (s), 124.7 (d, ^{1}J (C,P) = 14.9 Hz), 66.7 (d, ^{1}J (C,P) = 5.5 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 35.0.

O-benzyl di(naphthalen-2-yl)phosphinate (4f): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc = 2:1) gave product **4f** (169.3 mg, 0.415 mmol, 83 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 8.50-8.54 (m, 2H), 7.79-7.91 (m, 8H), 7.51-7.58 (m, 4H), 7.36-7.42 (m, 2H), 7.24-7.34 (m, 3H), 5.15 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ= 136.4 (d, ^{1}J (C,P) = 8.0 Hz), 135.0 (d, ^{1}J (C,P) = 2.4 Hz), 134.0 (d, ^{1}J (C,P) = 10.0 Hz), 132.6 (s), 132.4 (s), 129.1 (s), 128.6 (s), 128.5 (s), 128.4 (d, ^{1}J (C,P) = 1.9 Hz), 128.3 (d, ^{1}J

(C,P) = 137.0 Hz), 127.9 (s), 127.0 (s), 126.5 (s), 126.4 (s), 66.6 (d, ^{1}J (C,P) = 5.6 Hz); ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C): δ= 32.9. HRMS (EI) m/z: calcd. for $C_{27}H_{21}O_2P$: 408.1279, found: 408.1276.

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Supporting Information Available: Copies of ^{1}H, ^{13}C and ^{31}P NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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