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Base-promoted *O*-deprotonation/alkylation reaction of P(O)–OH compounds with alkyl halides

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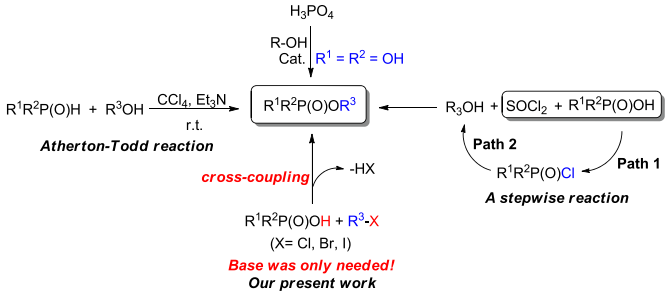
ABSTRACT

A novel base-promoted *O*-deprotonation/alkylation reaction of P(O)–OH compounds with alkyl halides has been developed. The protocol is practical, representing a simple way to produce a broad spectrum of functionalized phosphinates, phosphonates, and phosphates from basic starting materials with good to excellent yields. A plausible mechanism was proposed for this reaction.

1. Introduction

Organophosphorus compounds are valuable intermediates in organic synthesis.[1–7] They are used as structural components in pharmaceuticals,[3] polymers, photoelectric materials,[4] and biologically active compounds,[5] as well as acting as key intermediates for the preparation of phosphine ligands.[6] In recent years, there has been a growing interest in this kind of phosphorus compounds, and a variety of methods have been developed for their preparation using P(O)-H compounds as phosphorylation reagent. Nonetheless, reports on use of P(O)–OH compounds are rather limited.[7]

As depicted in Scheme 1, the most frequently employed method for their preparation is treating the P(O)-H compounds with nucleophiles under the conditions of Atherton–Todd reaction.[8a,b] The Atherton–Todd reaction is a classical synthetic method for the preparation of phosphates and related phosphorus compounds. Despite the method is versatile, it has shortcomings such as the lack of tolerance towards functional groups, and the generation of a large number of hazardous regents.[8] In 1962, Pollart et al. disclosed that in the presence of thionyl chloride, P(O)–OH can be easily converted to P(O)-Cl that reacts with nucleophiles (e.g., alcohols, phenols) to give the corresponding phosphates or phosphonates in a stepwise procedure.[9] Golubski also found that in the presence of crown ethers, the phosphinic acid salts reacted with alkyl halides efficiently, giving the corresponding alkylation products in good yields.[9f] In 2005, Ishihara et al. further demonstrated that the nucleophilic bases promoted the dehydrative condensation of phosphoric acid with alcohols.[10f,g] The P(O)–OH compounds exist widely as natural resources and can be easily prepared. They are commonly used as Brønsted acid catalyst in organic synthesis. Despite the P(O)–OH compounds are more stable than the P(O)-H compounds, studies on their activation are few.[10]



Scheme 1. Methods for the synthesis of phosphinates, phosphonates and phosphates.

Herein, we report the *O*-deprotonation/alkylation reaction of P(O)–OH compounds with alkyl halides under relatively mild conditions. The base-promoted system accommodates a wide

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0040-4020/

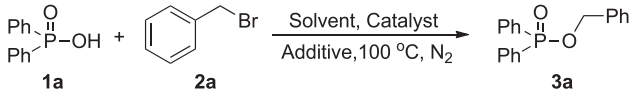
range of substituted alkyl halides, affording the generation of organophosphorus compounds in good to excellent isolated yield. From the standpoint of simplicity and economics, this synthetic method is superior to the traditional ones because there is no need to use P(O)-H and alcohols as starting materials.[7–10] Considering the wide utility of the resulting compounds, such a convenient and facile method for the synthesis of phosphinates, phosphonates, and phosphates from readily available P(O)–OH and alkyl halides will find wide application in the construction of biologically active molecules, catalysis ligands, and organophosphorus materials.

2. Results and discussion

In solvents such as toluene, DMF, DMSO, and ethanol, we detect no coupling product in the reaction of diphenyl phosphinic acid (**1a**) with benzyl bromide (**2a**) at 100 °C when 10 mol% of CuI is used as catalyst (Table 1, entries 1–4). Under similar conditions with CH_3CN being solvent, the expected coupling product, viz. benzyl phenyl (phenyl) phosphinate **3a**, is obtained in 82% yield (Table 1, entry 5). To our surprise, when Cs_2CO_3 is used alone in the absence of CuI, the reaction also proceeds efficiently with yield of the desired coupling product reaching 99% (Table 1, entry 6).We tried other bases such as Cs_2CO_3, Na_2CO_3, K_3PO_4, K_2CO_3, and $NaHCO_3$, and the yield of benzyl phenyl (phenyl) phosphinate **3a** is in the 13–72% range (Table 1, entries 6–10). Apparently, Cs_2CO_3 is the most suitable for this reaction, and 99% yield of **3a** is obtained at a molar ratio of diphenyl phosphinic acid to Cs_2CO_3 of 1:2 (Table 1, entry 6). When Cs_2CO_3 is reduced to 0.75 (1.5 equiv) and 0.5 (1.0 equiv) mmol, there is reduction of product yield to 82% and 68%, respectively. Furthermore, we observed that the reaction temperature has a significant influence on the reaction. At Cs_2CO_3 of 2 equiv, the yield of **3a** rises from 16% at 25 °C to 99% at 100 °C (Table 1, entries 6, 13–16). Since a rise of temperature to 120 °C results in a decrease of **3a** yield to 92% (Table 1, entry 17), we adopted 100 °C as the optimal temperature. Therefore, the optimal reaction conditions for the reaction are: 0.5 mmol of P(O)–OH compounds, 0.5 mmol of alkyl halides, 2.0 equiv of Cs_2CO_3 in CH_3CN (3 mL) at 100 °C under N_2 atmosphere with stirring for 12 h.

As shown in Table 2, the *O*-deprotonation/alkylation reaction can be applied to a variety of alkyl halides. Benzyl bromides bearing methyl, fluoro or bromo substituted functional groups react efficiently with diphenyl phosphinic acid to afford the corresponding coupling products in 91–96% isolated yields (Table 2, **3a**–**d**). In addition, 2-(bromomethyl) naphthalene also reacts with diphenyl phosphinic acid efficiently and gives (naphthalen-6-yl) methyl phenyl (phenyl) phosphinate **3e** as coupling product in 84% yield. We found that halogen-substituted alkanes such as 1-bromooctane, iodomethane, 1-bromobutane, 1-bromo-3-phenyl-propane, 1-bromo-3-methylbut-2-ene and 1-bromo-3-chloropropane are good substrates, giving coupling products (**3f**–**g**, **3i**–**l**) with diphenyl phosphinic acid in 82–94% yield. When 2-bromopropane (**2h**) is adopted as substrate, only 56% yield of the expected product isopropyl phenyl (phenyl) phosphinate **3h** is produced under the optimized conditions, but with the temperature raised to 120 °C, 88% yield of **3h** is obtained. This phenomenon is ascribed to the steric hindrance of the substrate.

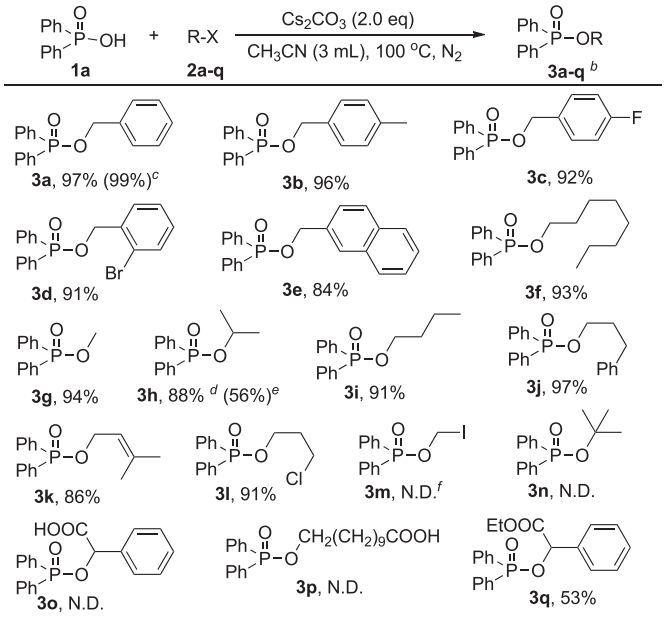
Table 1
Optimization of reaction conditions[a]



Entry	Cat. (10 mol%)	Solvent	Additive (2.0 equiv)	Yield (%)[b]
1	CuI	Toluene	Cs_2CO_3	N.D.
2	CuI	DMF	Cs_2CO_3	N.D.
3	CuI	DMSO	Cs_2CO_3	N.D.
4	CuI	CH_3OH	Cs_2CO_3	N.D.
5	CuI	CH_3CN	Cs_2CO_3	82%
6	None	CH_3CN	Cs_2CO_3	99%
7	None	CH_3CN	K_3PO_4	72%
8	None	CH_3CN	Na_2CO_3	27%
9	None	CH_3CN	K_2CO_3	58%
10	None	CH_3CN	$NaHCO_3$	13%
11	None	CH_3CN	Cs_2CO_3[c]	68%
12	None	CH_3CN	Cs_2CO_3[d]	82%
13	None	CH_3CN	Cs_2CO_3	87%[e]
14	None	CH_3CN	Cs_2CO_3	73%[f]
15	None	CH_3CN	Cs_2CO_3	52%[g]
16	None	CH_3CN	Cs_2CO_3	16%[h]
17	None	CH_3CN	Cs_2CO_3	92%[i]
18	18-crown-6 ether	CH_3CN	K_2CO_3	95%[j]

[a] Reaction conditions: diphenyl phosphinic acid (0.5 mmol), benzyl bromide (0.5 mmol), catalyst (10 mol%) and additive (2.0 equiv) in solvent (3 mL), under N_2 atmosphere with stirring at 100 °C for 12 h.
[b] Yield was determined by GC analysis, and dodecane was used as internal standard.
[c] Cs_2CO_3 (0.5 mmol, 1.0 equiv).
[d] Cs_2CO_3 (0.75 mmol, 1.5 equiv).
[e] 80 °C.
[f] 60 °C.
[g] 40 °C.
[h] 25 °C.
[i] 120 °C.
[j] 18-crown-6 ether (1 mol%), K_2CO_3 (0.5 mmol, 1.0 equiv).[9f]

Table 2
Scope of alkyl bromides[a]



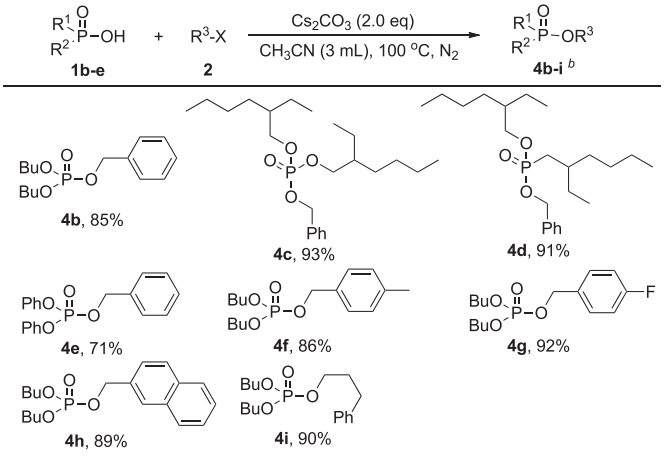
[a] Reaction conditions: diphenyl phosphinic acid (0.5 mmol), alkyl halides (0.5 mmol), and Cs_2CO_3 (2.0 equiv) in CH_3CN (3 mL), under N_2 atmosphere with stirring at 100 °C for 12 h. [b] Isolated yield. [c] GC yield. [d] 120 °C. [e] 100 °C. [f] N.D. = Not detected.

2-Bromo-2-methylpropane was also investigated for this reaction, but there is no product detected after having the reaction mixture stirred at 120 °C for 12 h (Table 2, **3n**). It was also observed that the use of di-iodomethane, 2-bromo-2-phenylacetic acid, and 11-bromounde-canoic acid as substrates does not result in coupling products (Table 2, **3m**, **3o**–**p**). It is deduced that under the adopted reaction conditions, the substrates (**2o** and **2p**) are in the state of cesium salts and do not react with phosphinic acid (**1a**) to give the expected final products. Interestingly, when ethyl 2-bromo-2-phenylacetate (**2q**, an ester) is applied instead, the corresponding

product (ethoxycarbonyl) (phenyl) methyl diphenyl phosphinate (**3q**) is generated in 53% yield.

We further investigated the reaction of different P(O)–OH compounds with alkyl halides under the optimized conditions. It is clear that both di-butyl phosphate (**1b**) and bis-(2-ethylhexyl) phosphate (**1c**) react with **2a** efficiently to give products **4a** and **4b** in 85 and 93% yields, respectively, (Table 3, entries 1–2). In addition, benzyl 2-ethylhexyl octan-3-ylphosphonate (**4c**) is obtained in 91% yield through the reaction of 2-ethylhexyl hydrogen-2-ethylhexylphosphonate (**1d**) with benzyl bromide (**2a**). However, when diphenyl phosphate (**1e**) reacts with benzyl bromide, only 71% yield of benzyl diphenyl phosphate (**4d**) is resulted, possibly due to the decomposition of **1e** at high temperature. In contrast, di-butyl phosphate (**1b**) shows good reactivity in the reaction, and gives the corresponding coupling products **4e**–**h** in 86–92% yields through the reaction with 1-(bromomethyl)-4-methylbenzene (**2b**), 1-(bromomethyl)-4-fluoro-benzene (**2c**), 2-(bromo-methyl) naphtha-ene (**2e**) and 1-bromo-3-phenyl-propane (**2j**), respectively.

Table 3
Scope of phosphinic acids[a]



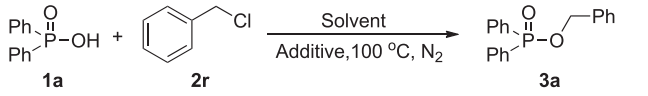
[a] Reaction conditions: P(O)-OH compounds (0.5 mmol), alkyl halides (0.5 mmol), and Cs_2CO_3 (2.0 equiv) in CH_3CN (3 mL), under N_2 atmosphere with stirring at 100 °C for 12 h. [b] Isolated yield.

As shown in Table 4, we further optimized the reaction of diphenyl phosphinic acid with benzyl chlorides. Various inorganic bases and organic base such as Cs_2CO_3, Na_2CO_3, K_2CO_3, $NaHCO_3$, NaOH, K_3PO_4 and Et_3N were screened for the reaction, and the yields of benzyl phenyl (phenyl) phosphinate **3a** are in the 2–71% range (Table 4, entries 1–8). According to the results, Cs_2CO_3 is the most suitable for the reaction, and the best loading is 2.0 equiv of substrates. On the other hand, the amount of CH_3CN shows no significant effect on the reaction (Table 4, entries 9–10). Since a rise of temperature from 100 to 120 °C results in a decrease of **3a** yield from 71% to 34% (Table 4, entries 1 and 11), we take 100 °C as the optimal temperature.

As depicted in Table 5, different substituted chloride (**2r**–**v**) react with diphenyl phosphinic acid efficiently under the optimized reaction conditions, giving the corresponding alkylation products (**3a**–**b**, **3r**–**s**) in 52–85% yields, respectively. It is hence demonstrated that alkyl chlorides can also be considered as good substrates in this reaction. Nonetheless, when 1-(chloromethyl)-4-nitrobenzene (**2v**) is applied as substrate, there is no production of the expected alkylation product 4-nitrobenzyl diphenyl phosphinate (**3t**).

We obtained dual-cross coupling products of ethylene bis-(diphenylphosphinate) (**5a**) and 1,3-propyl bis-(diphenylphosphinate) (**5b**) in 82% and 87% isolated yields from the reaction by employing 2-fold amount of diphenyl phosphinic acid (**1a**) to react

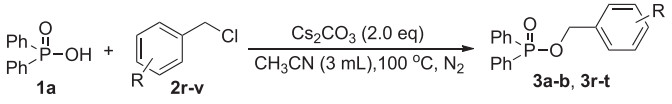
Table 4
Optimization of the reaction of diphenyl phosphinic acid with benzyl chloride in CH_3CN of different amounts[a]

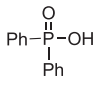
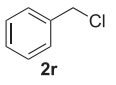
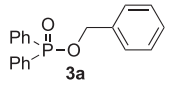
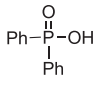
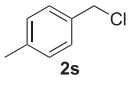
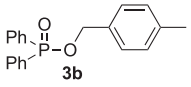
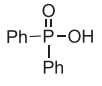
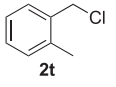
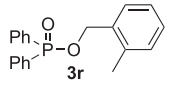
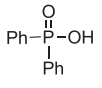
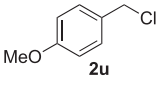
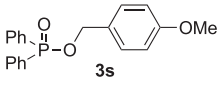
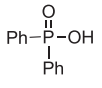
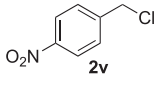
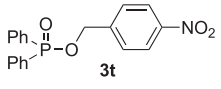


Entry	Temperature	Additive (2.0 equiv)	Yield (%)[b]
1	100 °C	Cs_2CO_3	71%
2	100 °C	Cs_2CO_3	49%[c]
3	100 °C	Na_2CO_3	2%
4	100 °C	K_2CO_3	32%
5	100 °C	$NaHCO_3$	2%
6	100 °C	NaOH	N.D.[d]
7	100 °C	K_3PO_4	27%
8	100 °C	Et_3N	17%
9	100 °C	Cs_2CO_3	40%[e]
10	100 °C	Cs_2CO_3	65%[f]
11	120 °C	Cs_2CO_3	34%

[a] Reaction conditions: diphenyl phosphinic acid (0.5 mmol), benzyl chloride (0.5 mmol), additive (2.0 equiv) in CH_3CN (3 mL), under N_2 atmosphere with stirring at 100 °C for 12 h.
[b] Yield was determined by GC analysis, and dodecane was used as internal standard.
[c] Cs_2CO_3 (0.5 mmol, 1.0 equiv).
[d] N.D.=Not detected.
[e] CH_3CN (1 mL).
[f] CH_3CN (5 mL).

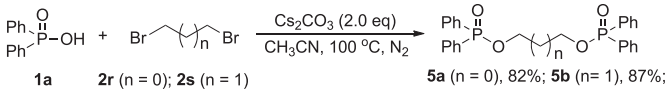
Table 5
Scope of benzyl chlorides[a]



Entry	P(O)–OH	R–Cl	Product	Yield[b]
1		 2r	 3a	71%
2		 2s	 3b	77%
3		 2t	 3r	85%
4		 2u	 3s	52%
5		 2v	 3t	N.D.[c]

[a] Reaction conditions: $Ph_2P(O)$–OH (0.5 mmol), alkyl chlorides (0.5 mmol), and Cs_2CO_3 (2.0 equiv) in CH_3CN (3 mL), under N_2 atmosphere with stirring at 100 °C for 12 h.
[b] Isolated yield.
[c] N.D.=Not detected.

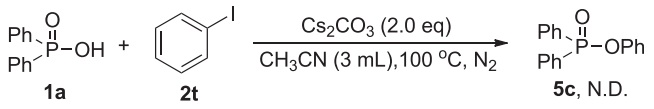
with compounds containing double-halogen substituted groups (Scheme 2, **2r**–**s**). It is worth pointing out that the compounds containing double phosphoryl functional groups are widely used in industry as flame-retardant materials.[11]



Scheme 2. Dual-cross coupling reaction of diphenyl phosphinic acid with dual-halogen-substituted alkanes.

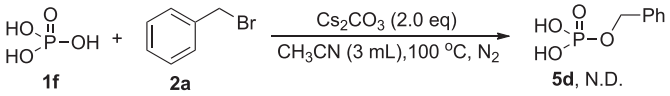
To test the applicability of the reaction further by reacting diphenyl phosphinic acid (**1a**) with iodobenzene (**2t**) but failed to obtain the expected product (Scheme 3). It is deduced that this is an SN_2 reaction and the aryl halides are not reactive enough (a result of p–π conjugative effect) to undergo nucleophilic attack towards **1a**.

We also investigated the reaction of phosphoric acid (**1f**) under



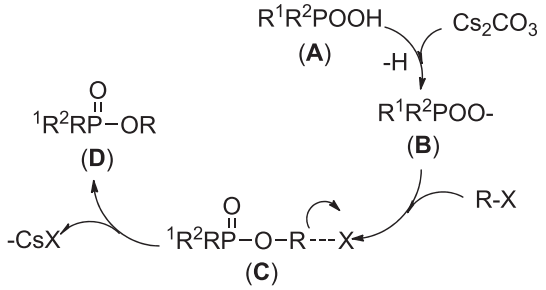
Scheme 3. Reaction of diphenyl phosphinic acid with iodobenzene.

the optimized reaction conditions but found no generation of phenyl dihydrogen phosphate (**5d**) (Scheme 4). It is deduced that phosphoric acid (**1f**) is highly reactive toward Cs_2CO_3, affording the corresponding inorganic bases (e.g., cesium dihydrogen phosphate, cesium hydrogen phosphate or cesium phosphate), which are not reactive enough to undergo nuclephilic attack by benzyl bromide.



Scheme 4. Reaction of phosphoric acid with benzyl bromide.

A possible mechanism for the base-promoted *O*-deprotonation/alkylation reaction of alkyl halides with P(O)–OH compounds is proposed as illustrated in Scheme 5. A stoichiometric amount of Cs_2CO_3 is needed to deprotonate the P(O)–OH compounds (**A**) to generate the corresponding anions (**B**) that are known to be good nucleophiles.[9f] With **B** attacking the alkyl halides from the back, there is the formation of transition state C, which is unstable in the presence of a base. Finally, what follow are the cleavage of the C–X bond and the generation of CsX to afford the cross-coupling product **D**.



Scheme 5. Proposed mechanism.

3. Conclusion

We have developed a divergent method for the preparation of phosphinates, phosphonates, and phosphates from P(O)–OH compounds with alkyl halides through the base-promoted *O*-deprotonation/alkylation reaction. The method avoids the use of air-sensitive reagents, allowing facile generation of a variety of functional substituted organophosphorus compounds from easily available P(O)–OH compounds. Considering the wide utility of the resulting compounds, the protocol will find wide application in the construction of biologically active molecules, catalysis ligands, and organophosphorus materials.

4. Experimental section

4.1. General information and materials

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. ^1H (400 MHz), ^{13}C (100 MHz), and ^{31}P (162 MHz) spectra were recorded on a 400 MHz 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 for the HRMS measurement, and the mass analyzer type is double-focusing.

4.2. General procedure

To a mixture of P(O)–OH compounds (0.5 mmol) and Cs_2CO_3 (1.0 mmol) in CH_3CN (3 mL), alkyl halide (0.5 mmol) was added under nitrogen atmosphere; the resulting mixture was stirred at 100 °C for 12 h. 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 as eluant.

*4.2.1. Benzyl phenyl (phenyl) phosphinate (**3a**).*[12a] Yield: 149.4 mg, (97%). Yellow oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.81–7.87 (m, 4H; Ar), 7.48–7.62 (m, 2H; Ar), 7.40–7.45 (m, 4H; Ar), 7.29–7.38 (m, 5H; Ar), 5.07 (d, J=6.4 Hz; 2H; $-OCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=136.2 (d, ^1J (C,P)=7.5 Hz; Ar), 132.2 (d, ^1J (C,P)=2.2 Hz; Ar), 131.6 (d, ^1J (C,P)=10.2 Hz; Ar), 131.2 (d, ^1J (C,P)=136.1 Hz; Ar–C–P), 128.6 (s; Ar), 128.4 (d, ^1J (C,P)=14.3 Hz; Ar), 128.2 (s; Ar), 127.8 (s; Ar), 66.2 (d, ^1J (C,P)=5.4 Hz; $-OCH_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=33.4.

*4.2.2. 4-Methyl-benzyl phenyl (phenyl) phosphinate (**3b**).*[12b] Yield: 154.5 mg, (96%). White solid, mp 91–93 °C. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.80–7.86 (m, 4H; Ar), 7.47–7.49 (m, 2H; Ar), 7.41–7.44 (m, 4H; Ar), 7.25 (d, J=7.6 Hz; 2H; Ar), 7.14 (d, J=8.0 Hz; 2H; Ar), 5.02 (d, J=6.8 Hz; 2H; $-OCH_2$), 2.32 (s, 3H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=138.1 (s; Ar), 133.3 (d, ^1J (C,P)=7.6 Hz; Ar), 132.2 (d, ^1J (C,P)=2.4 Hz; Ar), 131.7 (d, ^1J (C,P)=10.1 Hz; Ar), 131.4 (d, ^1J (C,P)=136.1 Hz; Ar–C–P), 129.2 (s; Ar), 128.5 (d, ^1J (C,P)=13.1 Hz; Ar), 128.1 (s; Ar), 66.2 (d, ^1J (C,P)=5.4 Hz; $-OCH_2$), 21.2 (s; $-CH_3$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=33.2.

*4.2.3. 4-Fluoro-benzyl phenyl (phenyl) phosphinate (**3c**).* Yield: 149.9 mg, (92%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.80–7.86 (m, 4H; Ar), 7.49–7.52 (m, 2H; Ar), 7.41–7.45 (m, 4H; Ar), 7.31–7.35 (m, 2H; Ar), 6.99–7.03 (m, 2H; Ar), 5.03 (d, J=7.2 Hz; 2H; $-OCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=162.6 (d, ^1J (C,F)=245.5 Hz; Ar–C–F), 132.3 (d, ^1J (C,P)=2.8 Hz; Ar), 132.2 (dd, ^1J (C,P)=3.2 Hz, ^2J (C,F)=3.1 Hz; Ar), 131.6 (d, ^1J (C,P)=10.2 Hz; Ar), 131.2 (d, ^1J (C,P)=135.9 Hz; Ar–C–P), 129.9 (d, ^1J (C,P)=8.3 Hz; Ar), 128.5 (d, ^1J (C,P)=13.2 Hz; Ar), 115.4 (d, ^1J (C,P)=21.5 Hz; Ar), 65.6 (d, ^1J (C,P)=5.4 Hz; $-OCH_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=33.6. HRMS calcd for $C_{19}H_{16}FO_2P$: 326.0872, found: 326.0867.

*4.2.4. 2-Bromobenzyl phenyl (phenyl) phosphinate (**3d**).*[12c] Yield: 176.1 mg, (91%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.84–7.89 (m, 4H; Ar), 7.44–7.52 (m, 8H; Ar), 7.27–7.31 (m, 1H; Ar), 7.13–7.16 (m, 1H; Ar), 5.15 (d, J=6.8 Hz; 2H; $-OCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=135.8 (d, ^1J (C,P)=7.8 Hz; Ar), 132.7 (s; Ar), 132.3 (d, ^1J (C,P)=2.7 Hz; Ar), 131.7 (d, ^1J (C,P)=10.2 Hz; Ar), 131.2 (d, ^1J (C,P)=136.0 Hz; Ar–C–P), 129.7 (s; Ar), 129.4 (s; Ar),

128.6 (d, ^{1}J (C,P)=13.1 Hz; Ar), 127.6 (s; Ar), 122.7 (s; Ar), 65.7 (d, ^{1}J (C,P)=4.0 Hz; −OCH_2); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=32.6.

*4.2.5. (Naphthalen-2-yl)methyl phenyl (phenyl) phosphinate (**3e**).* Yield: 150.4 mg, (84%). White solid, mp 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.76–7.88 (m, 7H; Ar), 7.41–7.48 (m, 8H; Ar), 5.21 (d, *J*=6.8 Hz; 2H; −OCH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=133.7 (d, ^{1}J (C,P)=7.4 Hz; Ar), 133.1 (d, ^{1}J (C,P)=2.2 Hz; Ar), 132.3 (d, ^{1}J (C,P)=2.7 Hz; Ar), 131.7 (d, ^{1}J (C,P)=10.1 Hz; Ar), 131.3 (d, ^{1}J (C,P)=135.8 Hz; Ar–C–P), 128.7 (s; Ar), 128.5 (s; Ar), 128.4 (s; Ar), 128.0 (s; Ar), 127.7 (s; Ar), 127.0 (s; Ar), 126.3 (s; Ar), 126.3 (s; Ar), 125.6 (s; Ar), 66.5 (d, ^{1}J (C,P)=5.4 Hz; −OCH_2); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=33.6. HRMS calcd for $C_{23}H_{19}O_2P$: 358.1123, found: 358.1128.

*4.2.6. Octyl phenyl (phenyl) phosphinate (**3f**).*[12d] Yield: 153.4 mg, (93%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.79–7.85 (m, 4H; Ar), 7.49–7.54 (m, 2H; Ar), 7.42–7.47 (m, 4H; Ar), 4.00–4.05 (m, 2H; OCH_2–), 1.69–1.76 (m, 2H; −CH_2), 1.26–1.41 (m, 10H; −CH_2), 0.85–0.89 (m, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=132.0 (d, ^{1}J (C,P)=2.7 Hz; Ar), 131.7 (d, ^{1}J (C,P)=136.2 Hz; Ar), 131.6 (d, ^{1}J (C,P)=10.0 Hz; Ar), 128.5 (d, ^{1}J (C,P)=13.0 Hz; Ar), 65.0 (d, ^{1}J (C,P)=6.0 Hz; OCH_2–), 31.7 (s; −CH_2), 30.5 (d, ^{1}J (C,P)=6.7 Hz; Ar), 29.7 (s; −CH_2), 29.1 (d, ^{1}J (C,P)=5.1 Hz; Ar), 25.6 (s; −CH_2), 22.6 (s; −CH_2), 14.1 (s; −CH_2); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=32.2.

*4.2.7. Methyl phenyl (phenyl) phosphinate (**3g**).*[12e] Yield: 109.1 mg, (94%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.79–7.85 (m, 4H; Ar), 7.50–7.55 (m, 2H; Ar), 7.43–7.48 (m, 4H; Ar), 3.77 (d, *J*=7.2 Hz, 3H; OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=132.2 (d, ^{1}J (C,P)=2.7 Hz; Ar), 131.6 (d, ^{1}J (C,P)=10.0 Hz; Ar), 130.9 (d, ^{1}J (C,P)=136.5 Hz; Ar–C–P), 128.5 (d, ^{1}J (C,P)=13.1 Hz; Ar), 51.5 (d, ^{1}J (C,P)=5.9 Hz; OCH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=34.3.

*4.2.8. Isopropyl phenyl (phenyl) phosphinate (**3h**).*[12f] Yield: 114.5 mg, (88%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.80–7.85 (m, 4H; Ar), 7.47–7.51 (m, 2H; Ar), 7.40–7.45 (m, 4H; Ar), 4.64–4.70 (m, 1H; OCH–), 1.34 (d, *J*=6.0 Hz, 6H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=132.3 (d, ^{1}J (C,P)=137.2 Hz; Ar–C–P), 131.9 (d, ^{1}J (C,P)=2.6 Hz; Ar), 131.5 (d, ^{1}J (C,P)=10.0 Hz; Ar), 128.4 (d, ^{1}J (C,P)=13.0 Hz; Ar), 70.1 (d, ^{1}J (C,P)=5.9 Hz; OCH–), 24.3 (d, ^{1}J (C,P)=4.1 Hz; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=30.8.

*4.2.9. Butyl phenyl (phenyl) phosphinate (**3i**).*[12g] Yield: 124.7 mg, (91%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.79–7.84 (m, 4H; Ar), 7.50–7.54 (m, 2H; Ar), 7.42–7.47 (m, 4H; Ar), 4.00–4.06 (m, 2H; OCH_2), 1.68–1.75 (m, 2H, −CH_2), 1.41–1.47 (m, 2H; −CH_2), 0.92 (t, *J*=7.2 Hz, 3H; CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=132.0 (d, ^{1}J (C,P)=2.3 Hz; Ar), 131.6 (d, ^{1}J (C,P)=136.4 Hz; Ar–C–P), 131.6 (d, ^{1}J (C,P)=10.0 Hz; Ar), 128.4 (d, ^{1}J (C,P)=13.0 Hz; Ar), 64.6 (d, ^{1}J (C,P)=6.0 Hz; OCH_2), 32.5 (d, ^{1}J (C,P)=6.6 Hz; −CH_2), 18.9 (s; −CH_2), 13.6 (s; −CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=32.2.

*4.2.10. 3-Phenylpropyl phenyl (phenyl) phosphinate (**3j**).*[12h] Yield: 163.1 mg, (97%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.79–7.84 (m, 4H; Ar), 7.40–7.50 (m, 6H; Ar), 7.23–7.26 (m, 2H; Ar), 7.14–7.17 (m, 3H; Ar), 4.03–4.10 (m, 2H; OCH_2), 2.72–2.75 (m, 2H, −CH_2), 1.41–1.47 (m, 2H; −CH_2), 2.01–2.07 m, 2H; −CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=141.1 (s; Ar), 132.2 (d, ^{1}J (C,P)=2.7 Hz; Ar), 131.6 (d, ^{1}J (C,P)=136.1 Hz; Ar–C–P), 131.6 (d, ^{1}J (C,P)=10.1 Hz; Ar), 128.6 (s; Ar), 128.5 (s; Ar), 128.4 (s; Ar), 126.0 (s; Ar), 64.2 (d, ^{1}J (C,P)=5.9 Hz; OCH_2), 32.1 (d, ^{1}J (C,P)=6.5 Hz; −CH_2), 31.9 (s; −CH_2); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=31.4.

*4.2.11. 3-Methylbut-2-enyl phenyl (phenyl) phosphinate (**3k**).*[12i] Yield: 122.9 mg, (86%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.80–7.85 (m, 4H; Ar), 7.42–7.52 (m, 6H; Ar), 5.39–5.43 (m, 1H; −CH=$C(CH_3)_2$), 4.54–4.57 (m, 2H; −OCH_2), 1.71 (s, 3H; −CH_3), 1.59 (s, 3H, −CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=139.1 (s; Ar), 132.0 (d, ^{1}J (C,P)=2.8 Hz; Ar), 131.8 (d, ^{1}J (C,P)=135.7 Hz; Ar–C–P), 131.7 (d, ^{1}J (C,P)=10.0 Hz; Ar), 128.4 (d, ^{1}J (C,P)=13.0 Hz; −CH=$C(CH_3)_2$), 119.6 (d, ^{1}J (C,P)=6.9 Hz; −CH=$C(CH_3)_2$), 61.6 (d, ^{1}J (C,P)=5.6 Hz; OCH_2), 25.7 (s; −CH_3), 18.0 (s; −CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=31.6.

*4.2.12. 3-Chloropropyl phenyl (phenyl) phosphinate (**3l**).*[12j] Yield: 133.7 mg, (91%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.79–7.84 (m, 4H; Ar), 7.51–7.55 (m, 2H; Ar), 7.43–7.48 (m, 4H; Ar), 4.16–4.21 (m, 2H; −OCH_2), 3.40 (t, *J*=6.4 Hz, 2H; −CH_2), 2.14–2.20 (m, 2H; −CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=132.1 (d, ^{1}J (C,P)=2.1 Hz; Ar), 131.4 (d, ^{1}J (C,P)=10.1 Hz; Ar), 131.0 (d, ^{1}J (C,P)=136.2 Hz; Ar–C–P), 128.4 (d, ^{1}J (C,P)=13.1 Hz; Ar), 61.4 (d, ^{1}J (C,P)=5.8 Hz; −OCH_2), 40.8 (s; −CH_2), 33.2 (d, ^{1}J (C,P)=5.4 Hz; CH_2); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=33.2.

*4.2.13. (Ethoxycarbonyl) (phenyl) methyl diphenyl phosphinate (**3q**).* Yield: 100.7 mg, (53%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.87–7.92 (m, 2H; Ar), 7.71–7.76 (m, 2H; Ar), 7.21–7.54 (m, 11H, Ar), 5.83 (d, *J*=10.0 Hz, 1H; −OCH), 4.06–4.16 (m, 2H; −OCH_2), 1.13 (t, *J*=6.8 Hz, 3H; −CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=169.0 (d, ^{1}J (C,P)=4.2 Hz; −C=O), 135.4 (d, ^{1}J (C,P)=4.8 Hz; Ar), 132.3 (d, ^{1}J (C,P)=2.8 Hz; Ar), 131.8 (d, ^{1}J (C,P)=2.6 Hz; Ar), 131.0 (d, ^{1}J (C,P)=136.0 Hz; Ar–C–P), 129.0 (s; Ar), 128.6 (s; Ar), 128.5 (d, ^{1}J (C,P)=7.4 Hz; Ar), 127.3 (s; Ar), 74.2 (d, ^{1}J (C,P)=5.0 Hz; −OCH), 61.7 (s; −OCH_2), 13.9 (s; −CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=34.0. HRMS calcd for $C_{22}H_{21}O_4P$: 380.1177, found: 380.1173.

*4.2.14. 2-Methyl-benzyl diphenyl phosphinate (**3r**).* Yield: 136.9 mg, (85%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.66–7.71 (m, 4H; Ar), 6.98–7.31 (m, 10H, Ar), 4.93 (d, *J*=6.0 Hz, 2H; −OCH_2), 2.15 (s, 3H; −CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=136.7 (s; Ar), 134.3 (d, ^{1}J (C,P)=7.6 Hz; Ar), 132.2 (d, ^{1}J (C,P)=2.7 Hz; Ar), 131.6 (d, ^{1}J (C,P)=10.1 Hz; Ar), 131.4 (d, ^{1}J (C,P)=135.7 Hz; Ar–C–P), 130.3 (s; Ar), 128.7 (s; Ar), 128.6 (s; Ar), 128.5 (d, ^{1}J (C,P)=13.0 Hz; Ar), 126.0 (s; Ar), 64.6 (d, ^{1}J (C,P)=5.4 Hz; −OCH), 18.8 (s; −CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=32.1. HRMS calcd for $C_{20}H_{19}O_2P$: 322.1123, found: 322.1121.

*4.2.15. 4-Methoxybenzyl diphenyl phosphinate (**3s**).* Yield: 87.9 mg, (52%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.71–7.76 (m, 4H; Ar), 7.39–7.43 (m, 2H; Ar), 7.31–7.35 (m, 4H; Ar), 7.13–7.17 (m, 1H; Ar), 6.73–6.85 (m, 3H; Ar), 4.94 (d, *J*=6.8 Hz, 1H; −OCH_2), 3.66 (s, 3H; −OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=159.7 (s; Ar), 137.8 (d, ^{1}J (C,P)=7.4 Hz; Ar), 132.3 (d, ^{1}J (C,P)=2.8 Hz; Ar), 131.7 (d, ^{1}J (C,P)=10.2 Hz; Ar), 131.3 (d, ^{1}J (C,P)=135.9 Hz; Ar–C–P), 128.6 (d, ^{1}J (C,P)=13.1 Hz; Ar), 120.1 (s; Ar), 113.6 (d, ^{1}J (C,P)=7.4 Hz; Ar), 66.2 (d, ^{1}J (C,P)=5.5 Hz; −OCH), 55.2 (s; −OCH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=32.5. HRMS calcd for $C_{20}H_{19}O_3P$: 338.1072, found: 338.1069.

*4.2.16. Benzyl dibutyl phosphate (**4b**).*[12k] Yield: 127.7 mg, (85%). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.32–7.41 (m, 5H; Ar), 5.06 (d, *J*=8.4 Hz, 2H; −OCH_2), 3.98–4.04 (m, 4H; −CH_2), 1.59–1.66 (m, 4H; −CH_2), 1.33–1.42 (m, 4H; −CH_2), 0.91 (t, *J*=7.2 Hz, 6H; −CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=136.1 (d, ^{1}J (C,P)=6.8 Hz; Ar), 128.5 (s; Ar), 128.4 (s; Ar), 127.8 (s; Ar), 68.9 (d, ^{1}J (C,P)=5.4 Hz; −OCH_2), 67.5 (d, ^{1}J (C,P)=6.0 Hz; −CH_2),

32.2 (d, ^1J (C,P)=6.9 Hz; $-CH_2$), 18.6 (s; $-CH_2$), 13.6 (s; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=0.39.

*4.2.17. Benzyl bis(2-ethylhexyl) phosphate (**4c**).* Yield: 191.6 mg, (93%). Colorless oil. (191.6 mg, 0.465 mmol, 93%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.32–7.41 (m, 5H; Ar), 5.07 (d, J=8.4 Hz, 2H; $-OCH_2$), 3.89–3.94 (m, 4H; $-OCH_2$), 1.51–1.55 (m, 2H; −CH), 1.26–1.38 (m, 16H; $-CH_2$), 0.85–0.90 (m, 12H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=136.1 (d, ^1J (C,P)=6.5 Hz; Ar), 128.5 (s; Ar), 128.3 (s; Ar), 127.3 (s; Ar), 69.6 (d, ^1J (C,P)=6.3 Hz; $-OCH_2$), 68.9 (d, ^1J (C,P)=5.5 Hz; $-OCH_2$), 40.0 (d, ^1J (C,P)=7.3 Hz; −CH), 29.8 (s; $-CH_2$), 28.8 (s; $-CH_2$), 23.1 (s; $-CH_2$), 22.9 (s; $-CH_2$), 14.0 (s; $-CH_3$) 10.8 (s; CH_3); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=0.62. HRMS calcd for $C_{23}H_{41}O_4P$: 412.2742, found: 412.2731.

*4.2.18. Benzyl 2-ethylhexyl 2-ethylhexylphosphonate (**4d**).* Yield: 180.2 mg, (91%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.31–7.40 (m, 5H; Ar), 5.06 (d, J=8.4 Hz, 2H; $-OCH_2$), 3.80–3.94 (m, 2H, $-OCH_2$), 1.68–1.77 (m, 2H; −CH), 1.26–1.49 (m, 18H; $-CH_2$), 0.82–0.88 (m, 12H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=136.7 (d, ^1J (C,P)=5.8 Hz; Ar), 128.5 (s; Ar), 128.2 (s; Ar), 127.8 (s; Ar), 67.2 (d, ^1J (C,P)=7.1 Hz; $-OCH_2$), 66.9 (d, ^1J (C,P)=6.3 Hz; $-OCH_2$), 40.1 (d, ^1J (C,P)=6.7 Hz; −CH), 34.0 (d, ^1J (C,P)=3.2 Hz; −CH), 33.5 (d, ^1J (C,P)=10.3 Hz; $-CH_2$), 29.9 (s; $-CH_2$), 29.7 (d, ^1J (C,P)=138.1 Hz; P−CH_2), 28.8 (s; $-CH_2$), 28.5 (s; $-CH_2$), 26.7 (d, ^1J (C,P)=9.8 Hz; $-CH_2$), 23.3 (s; $-CH_2$), 23.0 (s; $-CH_2$), 22.8 (s; $-CH_2$), 14.1 (s; $-CH_3$), 14.0 (s; $-CH_3$) 10.9 (d, ^1J (C,P)=1.3 Hz; $-CH_3$), 10.3 (d, ^1J (C,P)=2.0 Hz; $-CH_3$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ_1=33.24, δ_2=33.22. HRMS calcd for $C_{23}H_{41}O_3P$: 396.2793, found: 396.2797.

*4.2.19. Benzyl diphenyl phosphate (**4e**).*[12l] Yield: 120.8 mg, (71%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.29–7.36 (m, 10H; Ar), 7.17–7.25 (m, 5H; Ar), 5.25 (d, J=8.8 Hz, 2H; $-OCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=150.5 (d, ^1J (C,P)=7.1 Hz; Ar), 129.8 (s; Ar), 128.8 (s; Ar), 128.6 (s; Ar), 128.1 (s; Ar), 127.8 (d, ^1J (C,P)=10.6 Hz; Ar), 125.4 (s; Ar), 120.1 (d, ^1J (C,P)=4.8 Hz; Ar), 70.6 (d, ^1J (C,P)=5.9 Hz; $-OCH_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=−11.8.

*4.2.20. 4-Methyl benzyl dibutyl phosphate (**4f**).*[12m] Yield: 135.1 mg, (86%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.28 (d, J=8.2 Hz, 2H; Ar), 7.17 (d, J=7.6 Hz, 2H; Ar), 5.02 (d, J=8.0 Hz, 2H; $-CH_2$), 3.98–4.03 (m, 4H; $-OCH_2$), 2.35 (s, 3H; $-CH_3$), 1.58–1.65 (m, 4H; $-CH_2$), 1.35–1.42 (m, 4H; $-CH_2$), 0.91 (t, J=7.2 Hz, 6H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=138.3 (s; Ar), 133.1 (d, ^1J (C,P)=6.6 Hz; Ar), 129.2 (s; Ar), 128.0 (s; Ar), 69.0 (d, ^1J (C,P)=5.6 Hz; $-OCH_2$), 67.4 (d, ^1J (C,P)=6.0 Hz; $-CH_2$), 32.2 (d, ^1J (C,P)=6.9 Hz; $-CH_2$), 21.2 (s; $-CH_2$), 18.6 (s; $-CH_3$), 13.6 (s; $-CH_3$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=−0.70.

*4.2.21. 4-Fluoro benzyl dibutyl phosphate (**4g**).* Yield: 146.3 mg, (92%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.37–7.40 (m, 2H; Ar), 7.06 (t, J=8.0 Hz, 2H; Ar), 5.03 (d, J=8.4 Hz, 2H; $-CH_2$), 3.99–4.04 (m, 4H; $-OCH_2$), 1.59–1.66 (m, 4H; $-CH_2$), 1.33–1.43 (m, 4H; $-CH_2$), 0.92 (t, J=7.2 Hz, 6H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=162.7 (d, ^1J (C,F)=245.7 Hz; Ar−C−F), 132.0 (dd, ^1J (C,P)=6.4 Hz, ^2J (C,F)=6.5 Hz; Ar), 129.9 (d, ^1J (C,P)=8.3 Hz; Ar), 115.4 (d, ^1J (C,P)=21.5 Hz; Ar), 68.2 (d, ^1J (C,P)=5.5 Hz; $-OCH_2$), 67.5 (d, ^1J (C,P)=6.1 Hz; $-CH_2$), 32.2 (d, ^1J (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 °C): δ=−0.73. HRMS calcd for $C_{15}H_{24}FO_4P$: 318.1396, found: 318.1386.

*4.2.22. Dibutyl (naphthalen-2-yl)methyl phosphate (**4h**).* Yield: 155.8 mg, (89%). Yellow oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.77–7.84 (m, 4H; Ar), 7.44–7.51 (m, 3H; Ar), 5.22 (d, J=7.6 Hz, 2H; $-CH_2$), 4.00–4.05 (m, 4H; $-OCH_2$), 1.58–1.65 (m, 4H; $-CH_2$), 1.31–1.40 (m, 4H; $-CH_2$), 0.88 (t, J=7.2 Hz, 6H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=133.5 (d, ^1J (C,P)=6.6 Hz; Ar), 133.2 (s; Ar), 133.1 (s; Ar), 128.4 (s; Ar), 128.0 (s; Ar), 127.7 (s; Ar), 126.9 (s; Ar), 126.4 (s; Ar), 126.3 (s; Ar), 125.5 (s; Ar), 69.2 (d, ^1J (C,P)=5.5 Hz; $-OCH_2$), 67.6 (d, ^1J (C,P)=6.1 Hz; $-CH_2$), 32.2 (d, ^1J (C,P)=6.8 Hz; $-CH_2$), 18.6 (s; $-CH_2$), 13.6 (s; $-CH_3$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=−0.59. HRMS calcd for $C_{19}H_{27}O_4P$: 350.1647, found: 350.1638.

*4.2.23. Dibutyl 3-phenylpropyl phosphate (**4i**).* Yield: 147.8 mg, (90%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.26–7.30 (m, 2H; Ar), 7.17–7.19 (m, 3H; Ar), 4.02–4.07 (m, 6H; $-OCH_2$), 2.71–2.74 (m, 2H; $-CH_2$), 1.97–2.04 (m, 2H; $-CH_2$), 1.63–1.70 (m, 4H; $-CH_2$), 1.37–1.46 (m, 4H, $-CH_2$), 0.94 (t, J=7.2 Hz, 6H; $-CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=141.0 (s; Ar), 128.4 (s; Ar), 128.3 (s; Ar), 126.0 (s; Ar), 67.4 (d, ^1J (C,P)=6.1 Hz; $-OCH_2$), 66.7 (d, ^1J (C,P)=5.9 Hz; $-OCH_2$), 32.3 (d, ^1J (C,P)=6.8 Hz; $-CH_2$), 31.9 (d, ^1J (C,P)=7.0 Hz; $-CH_2$), 31.6 (s; $-CH_2$), 18.7 (s; $-CH_2$), 13.6 (s; $-CH_3$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=−0.66. HRMS calcd for $C_{17}H_{29}O_4P$: 328.1803, found: 328.1797.

*4.2.24. Ethylene bis(diphenylphosphinate) (**5a**).* Yield: 189.5 mg, (82%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.78–7.83 (m, 8H; Ar), 7.50–7.54 (m, 4H; Ar), 7.39–7.43 (m, 8H; Ar), 4.29 (d, J=4.0 Hz, 4H; $-OCH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=132.3 (d, ^1J (C,P)=2.7 Hz; Ar), 131.7 (d, ^1J (C,P)=10.2 Hz; Ar), 131.0 (d, ^1J (C,P)=145.3 Hz; Ar−C−P), 128.6 (d, ^1J (C,P)=13.2 Hz; Ar), 63.7 (dd, ^1J (C,P_1)=13.1 Hz, ^1J (C,P_2)=1.9 Hz; $-OCH_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=32.8. HRMS calcd for $C_{26}H_{24}O_4P_2$: 462.1150, found: 462.1124.

*4.2.25. 1,3-Propyl bis(diphenylphosphinate) (**5b**).* Yield: 207.1 mg, (87%). Colorless oil. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ=7.77–7.82 (m, 8H; Ar), 7.47–7.51 (m, 4H; Ar), 7.39–7.43 (m, 8H; Ar), 4.19–4.24 (m, 4H; OCH_2), 2.12–2.15 (m, 2H, $-CH_2$); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ=132.2 (d, ^1J (C,P)=2.8 Hz; Ar), 131.5 (d, ^1J (C,P)=10.1 Hz; Ar), 131.2 (d, ^1J (C,P)=136.1 Hz; Ar−C−P), 128.4 (d, ^1J (C,P)=12.8 Hz; Ar), 60.9 (d, ^1J (C,P)=5.7 Hz; $-OCH_2$), 31.6 (t, ^1J (C,P)=6.7 Hz; $-CH_2$); ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C): δ=31.8. HRMS calcd for $C_{27}H_{26}O_4P_2$: 476.1306, found: 476.1281.

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Supplementary data

Supplementary data associated with this article can be found at http://dx.doi.org/10.1016/j.tet.2014.10.013. These data include MOL files and InChiKeys of the most important compounds described in this article.

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