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LiI/TBHP Mediated Oxidative Cross Coupling of P(O)-H Compounds with Phenols and Various Nucleophiles: Direct access for the Synthesis of Organophosphates

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Dedication ((optional)

Abstract: An efficient and mild method for the direct phosphorylation of phenols, alcohols and amines with P(O)-H has been reported by LiI/TBHP mediated oxidative cross coupling reaction. Moreover, this protocol extended to β-ketoesters for the synthesis of enol phosphates using H-phosphonates. Notably, this developed method applied for the synthesis of organopesticides such as paraoxon, cyanophos and methyl parathion. The key features of this protocol are mild conditions, short reaction time, good functional group tolerance and broad substrate scope.

Introduction

Phosphate esters have been found in a variety of biological molecules such as nucleic acids, proteins, carbohydrates, lipids, coenzymes and steroids.[1] They are also essential constituents in many insecticides and herbicides.[2] Phosphorylation of alcohol group in inositols and glycerols plays an essential role in many physiologically important processes.[3] In addition, phosphate derivatives are commonly prepared in order to increase the aqueous solubility of alcohols in prodrugs.[4ï 6] Recent discoveries of numerous natural organophosphates endowed with interesting activities in both agricultural and medicinal fields have encouraged the development of synthetic analogues.[12,13] As illustrated in Figure 1, paraoxon, cyanophos, methyl parathion, temefos, coroxon and DEPFMU are well known pesticides.[14] Moreover, Phosphate esters are tunable reagents and functional groups in organic synthesis.[7] Further, they have also been widely exploited as organo catalysts,[8] coupling partners [9] and directing groups in Pd-catalyzed cross coupling reactions.[10] Therefore, organophosphorus compounds attract increasing attention from academic and industrial researchers.[11]

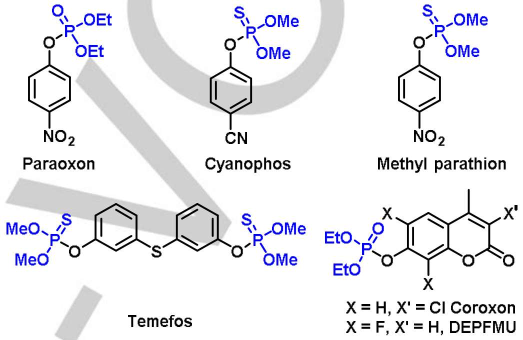
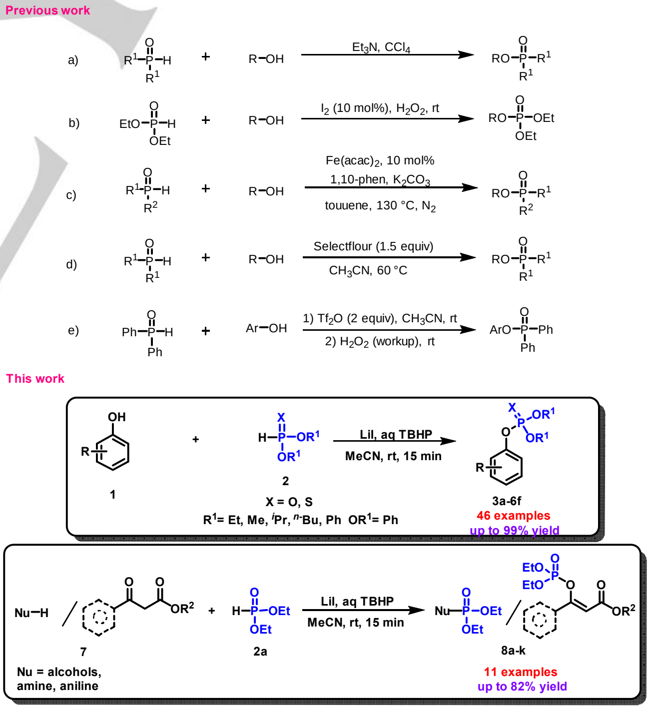


Figure 1. Pesticides bearing phosphate and thiophosphate



Scheme 1. Methods for phosphates synthesis.

Traditionally organophosphates are synthesized by using prefunctionalized phosphoryl chlorides (P(O)-Cl) with various nucleophiles *via* nucleophilic substitution method.[15] Over the past few years, cross coupling reactions played a significant role for the synthesis of organophosphates.[16] Atherton and Todd

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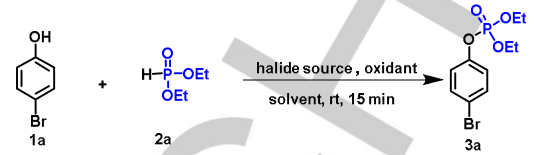
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) introduced the phosphorylation of alcohols and amines by treating with simple dialkyl phosphites (P(O)-H) as a phosphorylating reagent in the presence of triethylamine and CCl_4 (Scheme 1a).[17] In 2013, Prabhu and co-workers developed a metal free phosphorylation of alcohols and amines *via* cross dehydroganative coupling reaction (CDC) in the presence of I_2/ H_2O_2 catalytic system (Scheme 1b).[18] Later, Chen and Han group reported iron catalyzed CDC reaction for the preparation of phosphate esters with P(O)ī H compounds and alcohols at high temperature (Scheme 1c).[19] Similalry, Chen *et al.* prepared phosphinic acids or phosphinates in the presence of Selectfluor *via* a one-pot coupling process of secondary phosphine oxides with water or alcohols (Scheme 1d).[20] Recently, Lu group reported an electrophilic phosphination of arenols with diphenylphosphine oxides leading to the formation of diphenyl aryl phosphinates in the presence of Tf_2O/ H_2O_2 system (Scheme 1e).[21] In addition, different phosphorylating reagents have been used for the synthesis of variety organophosphates.[22] However, most of these methods suffers from multistep synthesis, low functional group tolerance and substrate limitation.[23,24] Hence, the direct phosphorylation of nucleophiles with good functional group tolerance, broad substrate scope and high yields are highly desirable.

In continuation of our efforts on oxidative cross coupling reactions,[25] we herein describe the LiI/TBHP mediated oxidative cross coupling of phenol derivatives, alcohols, amines, and enols with P(O)-H for the direct synthesis of organophosphates.

Results and Discussion

Initial investigations were initiated with 1 mmol of 4-bromophenol **1a** and 3 mmol of diethyl phosphite **2a** as model substrates in presence of 1 equiv of TBAI and 3 equiv of 70% aq TBHP in MeCN (2mL), which afforded the corresponding organophosphate **3a** in 10% yield (Table 1, entry 1). Subsequently change of halide source from TBAI to KI has improved the product yield **3a** to 18% and extending the reaction time under the similar conditions could not increase the yield of **3a** (entries 2 and 3). The formation of product could not be observed either the use of stochiometric amount of I_2 in the presence of TBHP (entry 4) or catalytic amount of I_2 in the presence of H_2O_2 as an oxidant (entry 5).[18] However, it was delighted to see the product **3a** in 87% yield (entry 6) when 1 equivalent of LiI was used as a iodide source. Further, investigations with other iodide sources such as NaI has furnished **3a** in 38%, while no product formation was observed with CsI (entries 7 and 8). For this particular reaction it was oberved that LiI is superior to other alkali iodides. When LiI was replaced with other lithium halides such as LiCl and LiBr, the reaction was not observed with the former, whereas the later furnished the product **3a** only in 10% (entries 9 and 10). Use of other oxidants such as H_2O_2, O_2 and *m*-CPBA were not effective for this transformation (entries 11-13). To scrutinize the solvent effect, the reactions were performed in different solvents. In case of MeOH as a solvent, **3a** was formed only in trace amount and notably we observed the formation of diethyl methyl phosphate ($(EtO)_2P(O)OMe$) product in 65% yield, was confirmed by ^1H NMR (entry 14). The reaction was facile in other solvents such as DCM and toluene and afforded the product **3a** in comparable yields (entries 15 and16). Furthermore, catalytic amount of LiI was unsuccessful in promoting the reaction under standard conditions and which was true even at elevated

Table 1. Optimization of the reaction conditions.[a]



Entry	Halide source (equiv)	Oxidant	Solvent	Yield[b] (%)
1	TBAI (1)	TBHP	MeCN	10
2	KI (1)	TBHP	MeCN	18
3[c]	KI (1)	TBHP	MeCN	18
4	I_2 (1)	TBHP	MeCN	0
5[d]	I_2 (0.1)	H_2O_2	-----	0
6	LiI (1)	TBHP	MeCN	87
7	NaI (1)	TBHP	MeCN	38
8	CsI (1)	TBHP	MeCN	0
9	LiCl (1)	TBHP	MeCN	0.
10	LiBr (1)	TBHP	MeCN	10
11	LiI (1)	H_2O_2	MeCN	0
12	LiI (1)	O_2	MeCN	0
13	LiI (1)	*m*-CPBA	MeCN	0
14	LiI (1)	TBHP	MeOH	3
15	LiI (1)	TBHP	DCM	85
16	LiI (1)	TBHP	Toluene	85
17	LiI (0.1)	TBHP	MeCN	0
18	LiI (0.3)	TBHP	MeCN	0
19	LiI (0.5)	TBHP	MeCN	0
20[e]	LiI (0.1)	TBHP	MeCN	0
21[f]	**LiI (1)**	**TBHP**	**MeCN**	**85**
22	-----	TBHP	MeCN	0
23	LiI (1)	-----	MeCN	0

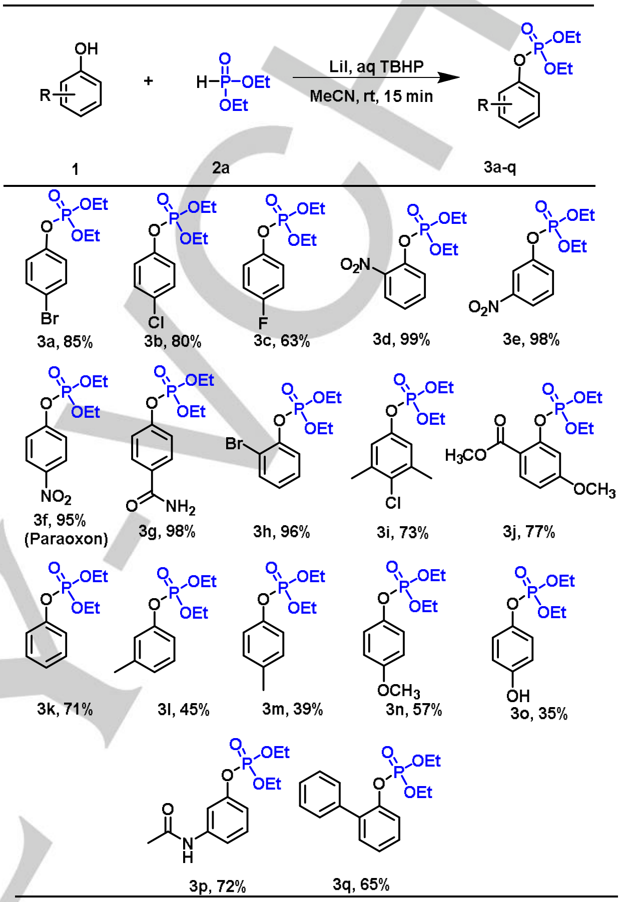
[a] Reaction conditions: **1a** (1 mmol), **2a** (3 mmol), halide source (1 mmol), oxidant (3 mmol), solvent (2 mL), rt, 15 min. [b] Yield based on isolated product. [c] Reaction was stirred for 24 h. [d] **1a** (0.72 mmol), **2a** (2.17 mmol), H_2O_2 (1 equiv), 24 h. [e] Reaction was carried out at 80 °C. [f] 1 equiv of **2a** was used.

temperature (entries 16-19). It is noteworthy to mention that, when 1 mmol of **2a** was reacted with 1 mmol of **1a**, the reaction worked smoothly and the product **3a** was afforded in 85% yield (entry 20), which was finalized as the optimized condition for further studies. While in the blank experiments such as absence of halide source and absence of oxidant, there was no product formation (Table 1, entries 21 and 22). These blank experiments clearly show that both halide source and oxidant play an important role in this transformation.

The generality and substrate scope of the reaction was studied under optimized conditions with various substituted phenols as shown in Table 2. The phenols bearing halogen functional groups such as 4-Br, 4-Cl and 4-F were well tolerated and afforded the required products **3a-c** in good yields. The substitution of a nitro group at *ortho, meta* and *para* on phenols did not influence much on the product formation **(3d-f,** 99%, 98% and 95%**)**. The synthesis of a pesticide **3f** (paraoxon) was accomplished in excellent yield using this method. Similarly, 4-hydroxybenzamide and 2-bromophenol underwent the reaction and obtained the desired products in excellent yields **(3g** and **3h)**. The substrates containing both electron donating as well as withdrawing groups in the same molecule were also well tolerated and furnished the products in good yields **(3i** and **3j)**. A simple phenol could react well with **2a** and afford the product **3k** in good yield. An electron donating substrates such as *m*-cresol and *p*-cresol provided the products in lower yields **(3l** and **3m)**. The oxidative coupling product of 4-methoxyphenol with **2a** was obtained in moderate yield **(3n)**, whereas the hydroquinone could manage to give the lower yield of the product **(3o)**. To our delight, acetamide group was well tolerated and reacted efficiently to afford the desired product in 72% yield **(3p)**. When 2-phenylphenol was subjected to the standard reaction conditions, the respective product was obtained in 65% yield **(**Table 2, **3q)**.

In addition, the scope of phosphites, phosphine oxide, phosphinate and dimethy thiophosphite were investigated under optimized reaction conditions as shown in Table 3. The reaction of 4-bromophenol with dimethyl phosphite **2b**, diisopropyl phosphite **2c** and di-*n*-butyl phosphite **2d** afforded the corresponding products in low to good yields **(4a-4c)**. Treatment of 3-chlorophenol with **2c** provided **4d** in 80% yield. The substrates having electron withdrawing and donating groups in the same molecule reacted with **2c** and **2d** and the desired products were obtained in 82% yield (**4e** and **4f***)*. When *ortho*-nitrophenol was treated with **2d**, the corresponding product was obtained in 90% yield **(4g)**, while the same substrate reacted with diphenyl phosphite and diphenylphosphine oxide, respective products **4h** and **4i** were obtained in poor yields. This could be due to the presence of unreacted H-phosphonate. To our delight, phosphorylation of **1a** was observed with ethyl phenylphosphinate and the corresponding product obtained in 45% yield **(4j)**. Electron rich substrates such as *m*-cresol and 4-methoxyphenol when reacted with **2c**, the products were obtained in 30% and 45% yields respectively **(4k** and **4l)**. Furthermore, this methodology was extended to the synthesis of pesticides such as cyanophos **4m** and methyl parathion **4n** where the produts were obtained in 43% and 58% yields respectively. The reaction was compatible with thiodiphenol and the corresponding product **4o** was obtained in lower yield (Table 3).

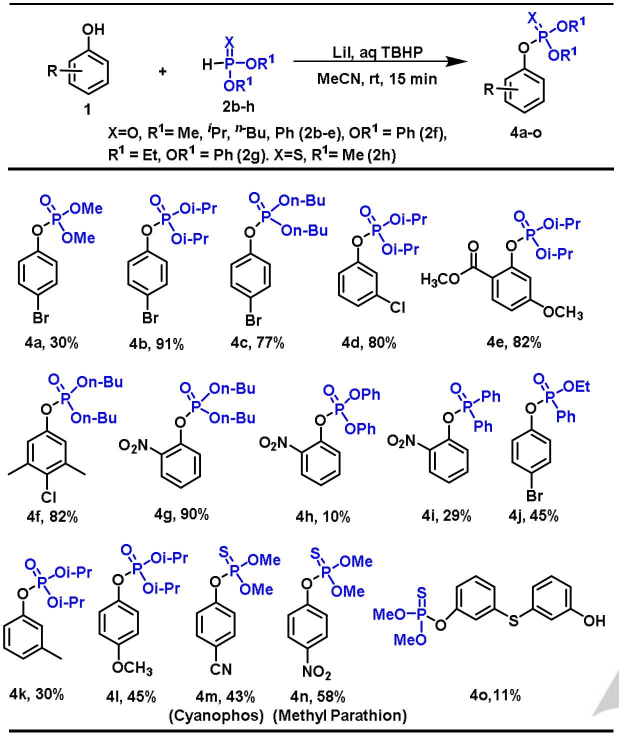
Table 2. Substrate Scope of Phenols with diethyl phosphite.[a,b]



[a] Reaction conditions: **1** (1 mmol), **2a** (1 mmol), LiI (1 mmol), 70% aq TBHP (3 mmol), MeCN (2 mL), rt, 15 min. [b] Yields based on isolated product.

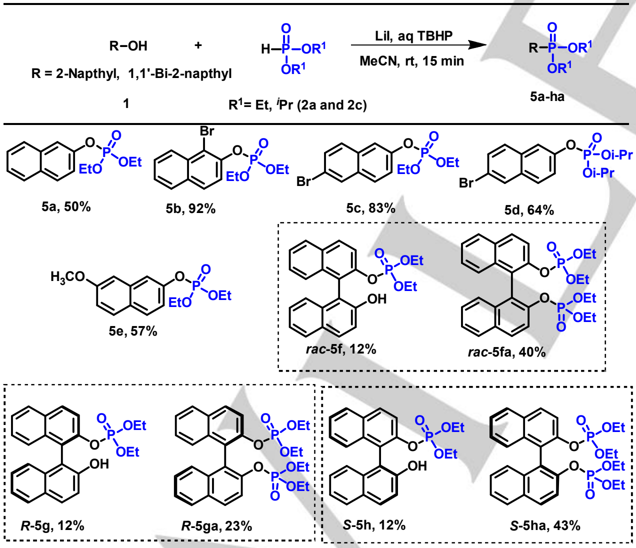
Furthermore, the substrate scope was extended to 2-naphthols and 1,1'-bi-2-naphthols (Table 4, **5a-5ha**). While 2-naphthol furnished the desired product in moderate yield, the electron withdrawing analogues such as 1-bromo-2-naphthol and 6-bromo-2-naphthol provided the products in good yields **(5a-c)**. The 6-bromo-2-naphthol with **2c** under standard reaction conditions, the corresponding product was isolated in 64% yield **(5d)**. When 7-methoxy naphthol was reacted with **2a** the product **5e** was obtained in 57% yield. In case of racemic binaphthol a mixture of monophosphorylation product **5f** (12%) and diphosphorylation product **5fa** (40%) were obtained. Interestingly, the reaction of enantiopure *R* and *S*-binaphthols under standard reaction conditions, furnished the corresponding enantiopure mono and diphosphorylation products *R*-**5g**, *R*-**5ga**, *S*-**5h** and *S*-**5ha** in low to moderate yields (Table 4).

Table 3. Substrate scope of phenols with different phosphites, phosphine oxide, phosphinate and dimethyl thiophosphite. [a,b]



[a] Reaction conditions: **1** (1 mmol), **2** (1 mmol), LiI (1 mmol), 70% aq TBHP (3 mmol), MeCN (2 mL), rt, 15 min. [b] Yields based on isolated product.

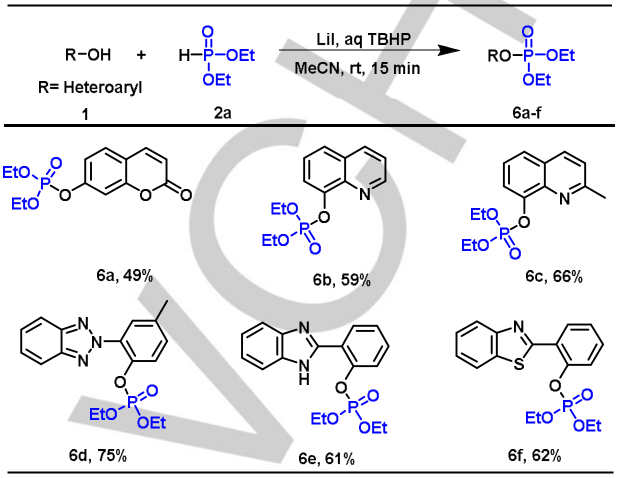
Table 4. Substrate scope of 2-naphthols and 1,1'-Bi-2-naphthols with diethyl and diisopropyl phosphite. [a,b]



[a] Reaction conditions: **1** (1 mmol), **2a & 2c** (1 mmol), LiI (1 mmol), 70% aq TBHP (3 mmol), MeCN (2 mL), rt, 15 min. [b] Yields based on isolated product.

The treatment of 7-hydroxy coumarin, 8-quinolinol and 2-methyl-8-quinolinol with **2a** resulted the corresponding products in moderate to good yields (Table 5, **6a-6c**). Similarly, the reactions of benzotriazolyl-*p*-cresol, benzimidazolyl-phenol and hydroxyphenyl-benzothiazole with **2a** furnished the respective products in good yields (Table 5, **6d-6f**).

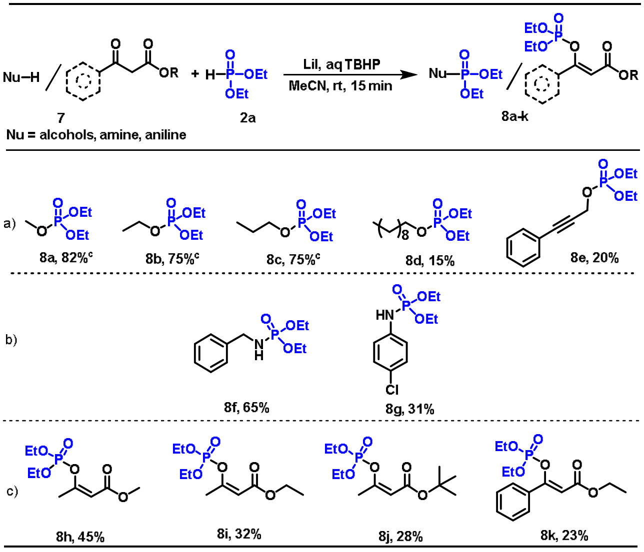
Table 5. Substrate scope of hydroxylated heteroarenes. [a,b]



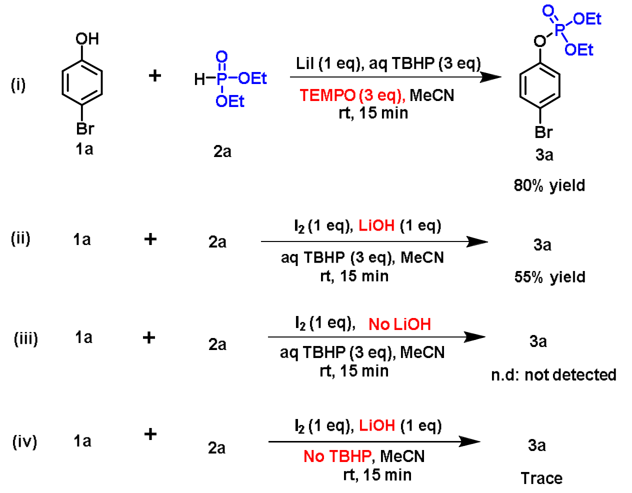
[a] Reaction conditions: **1** (1 mmol), **2a** (1 mmol), LiI (1 mmol), 70% aq TBHP (3 mmol), MeCN (2 mL), rt, 15 min. [b] Yields based on isolated product.

In addition to phenols, aliphatic alcohols were also investigated under the standard reaction conditions. When the reaction was performed with methanol, ethanol and propanol using **2a,** the corresponding coupled products were obtained in good yields **(**Table 6a, **8a-8c)**. Similarly, decanol and 3-phenyl propargyl alcohol with **2a** resulted phosphorylation products in poor yields **(**Table 6a, **8d** and **8e)**. To our delight, benzylamine and 4-chloro aniline were also smoothly provided N-P bond formation products with **2a** under standard reaction conditions in moderate to good yields **(**Table 6b, **8f** and **8g)**. There was no reaction with thiophenol and the starting material remains intact. Based on our previous reports with β-ketoesters and dimethyl formamide[26] we investigated the scope of β-ketoesters with **2a** under the standard reaction conditions and obtained the enol phosphates in low to moderate yields **(**Table 6c**, 8h-8k)**.

Table 6. Substrate scope of different nucleophiles with diethyl phosphite. [a,b]



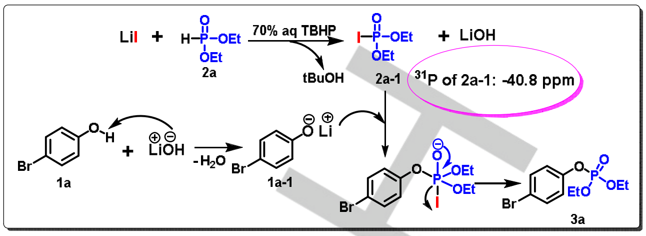
[a] Reaction conditions: **7** (1 mmol), **2a** (1 mmol), LiI (1 mmol), 70% aq TBHP (3 mmol), MeCN (2 mL), rt, 15 min. [b] Yields based on isolated product. [c] **7** (10 mmol), neat.



Scheme 2. Control experiments

To investigate the mechanism, we have conducted the control experiments (Scheme 2). The reaction of **1a** with **2a** in presence of 3 equiv TEMPO under the standard reaction conditions the product **3a** was obtained in 80% yield (Scheme 2, i). This result indicates that the reaction may not be proceeding through a radical path way. Next, the reaction of **1a** (1 mmol) with **2a** (1 mmol) in the presence of 1 equiv of I_2 and 1 equiv of LiOH as a base using 3 equiv of TBHP, resuted the product **3a** in 55% yield (Scheme 2, ii)**.** This reaction supports our interpretation that *in situ* generated LiOH base and I_2 might be involved in the transformation of **1a** and **2a** to **3a**. Further, we did not detect any product formation in the absence of LiOH and an oxidant (Scheme 2, iii and iv). These results supports that the role of both lithium iodide and oxidant might be crucial. Moreover, we have also done the further investigation on the mechanistic studies using NMR experiments. The reaction of diethyl phosphite when treated in an NMR tube with LiI and TBHP in toluene at room temperature resulted in the formation of a product, which was found to be resonating at -40.8 ppm as per ^{31}P NMR. It was then identified and compared as an intermediate diethyl phosphoroiodate based on previous ^{31}P NMR data[27] (please see the supporting information).

Based on our own control experiments and previous reports,[27] we have proposed a plausible mechanism as shown in Scheme 3. Initially, LiI reacts with **2a** in the presence of aq TBHP and generates diethyl phosphoroiodate intermediate **(2a-1)** and LiOH. Subsequentially, the newly formed LiOH may abstract the proton from **1a** and results 4-bromo lithium phenoxide **(1a-1)** and water. Finally, **1a-1** reacts with **2a-1** to obtain the corresponding product **3a** (Scheme 3).



Scheme 3. Plausible mechanism

Conclusions

In conclusion, we have developed an efficient and mild method for the direct phosphorylation of phenols, alcohols and amines by LiI/TBHP mediated oxidative cross coupling reaction. Moreover, this protocol extended to ϐ-ketoesters for the synthesis of enol phosphates using H-phosphonates. Notably, this developed method applied for the synthesis of organo pesticides such as paraoxon, cyanophos and methyl parathion. The main features of this protocol are mild conditions, short reaction time, good functional group tolerance and broad substrate scope.

Experimental Section

All chemicals were purchased from Sigma-Aldrich, Alfa Aeser and Avra Chemicals, Pvt. Ltd. India and used as received. Silica gel (100ï 200 mesh) was used for column chromatography and thin-layer chromatography was performed on Merck-pre-coated silica gel 60-F_{254} plates and visualized by UV-light and developed by Iodine. All the other chemicals and solvents were obtained from commercial sources and purified using standard methods. All ^{1}H and ^{13}C were recorded on a Avance-300, Avance-400, Inova-500 MHz Spectrometer. Chemical shifts (δ) are reported in ppm, using TMS (δ =0) as an internal standard in $CDCl_3$ and 85% H_3PO_4 as external standard for ^{31}P NMR (202 MHz). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The coupling constants (*J*) are reported in Hertz (Hz). The IR values are reported in reciprocal centimeters (cm^{-1}). Mass spectral data were compiled using Electron Spray Ionization mass spectrometer (ESI-MS) and High Resolution Mass Spectrometer (HRMS).

General Procedure for the Synthesis of organophosphates

A mixture of Phenol derivatives and other nucleophiles such as alcohols, amines and ϐ-ketoesters (1.0 mmol), H-phosphonate (1 mmol) and LiI (1 mmol) were taken in 2.0 mL of MeCN in a single-neck reactor. To this stirred solution 3 equiv. of 70% aq. TBHP was added at room temperature, in an open air atmosphere (**Caution:** It is observed that the reaction is exothermic in nature). The reaction was stirred up to 15 min and the completion of the reaction was monitored by thin layer chromatography (TLC). The reaction mixture was diluted with ethyl acetate and washed with sodium thiosulphate. The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate) to afford the pure product. The product was confirmed by ^{1}H, ^{13}C, ^{31}P NMR, IR, ESI-MS and HRMS analysis.

4-Bromophenyl diethyl phosphate (3a):
Yellow oil, 263 mg (85%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.45 (d, J = 9.0 Hz, 2H), 7.12 (d, J = 9.0 H$_Z$, 2H), 4.17-4.25 (m, 4H), 1.35 (t, J = 7.0 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 149.7 (d, J = 7.2 Hz), 132.6, 121.7 (d, J = 4.54 Hz), 117.8, 64.7 (d, J = 5.4 Hz), 16.0 (d, J = 7.2 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.47; IR v_{max} cm^{-1}: 2981, 2913 2377, 1583, 1485, 1275, 1217, 1164, 1028, 957, 928, 833, 779, 541; MS (ESI) m/z = 331 (M+Na)$^+$; HRMS m/z (ESI) calculated for C$_{10}$H$_{14}$O$_4$BrNaP (M+Na)$^+$: 330.97053, found: 330.97012.

4-Chlorophenyl diethyl phosphate (3b):
Red oil; 211 mg (80%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.28 (t, J = 9.0 Hz, 2H), 7.17(d, J = 8.3 Hz, 2H), 4.16-4.26 (m, 4H), 1.35 (t, J = 6.7 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 149.2 (d, J = 6.3 Hz), 130.2, 129.6, 121.3 (d, J = 4.5 Hz), 64.7 (d, J = 5.4 Hz), 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.3. IR v_{max} cm^{-1}: 2982, 2911, 2378, 1583, 1488, 1273, 1218, 1164, 1028, 959, 928, 837, 784, 641, 547; MS (ESI) m/z = 287 (M+Na)$^+$; (ESI-HRMS) calculated for C$_{10}$H$_{14}$O$_4$ClNaP (M+Na)$^+$: 287.02104, found: 287.02051.

4-Fluorophenyl diethyl phosphate (3c):
Red oil; 157 mg (63%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.18 (d, J = 5.4 Hz, 2H), 7.01 (d, J = 11.7 Hz, 2H), 4.16-4.27 (m, 4H), 1.35 (t, J = 7.1 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 160.5, 158.6, 146.5 (d, J = 6.3 Hz), 121.3 (dd, $J_{C\text{-}P}$ = 4.5 Hz, $J_{C\text{-}F}$ = 3.6 Hz), 116.2, 116.0, 64.6 (d, J = 5.4 Hz), 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm) ŭ -6.0; IR v_{max} cm^{-1}: 2896, 2916, 2377, 1503, 1276, 1197, 1093, 1028, 958, 842, 762, 559; MS (ESI) m/z = 271 (M+Na)$^+$; (ESI-HRMS) calculated for C$_{10}$H$_{14}$O$_4$FNaP (M+Na)$^+$: 271.05059, found: 271.05020.

Diethyl (2-nitrophenyl) phosphate (3d):
Yellow oil; 273 mg (99%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.58 (d, J = 7.9 Hz, 1H), 7.47 (d, J = 8.2 Hz, 1H), 7.29 (t, J = 8.2 Hz, 1H), 7.04 (t, J = 8.8 Hz, 1H), 4.24-4.32 (m, 4H), 1.37 (t, J = 7.1 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 147.9 (d, J = 4.5 Hz), 133.5, 128.6, 125.9, 121.0, 114.39 (d, J = 8.1 Hz), 65.0 (d, J = 6.3 Hz), 16.0 (d, J = 7.2 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.9; IR v_{max} cm^{-1}: 2989, 2914, 2379, 1604, 1531, 1483, 1354, 1279, 1238, 1164, 1090, 1027, 955, 928, 848, 780, 656, 547; MS (ESI) m/z = 276 (M+H)$^+$; (ESI-HRMS) calculated for C$_{10}$H$_{15}$O$_6$NP (M+H)$^+$: 276.06315 found: 3276.06244.

Diethyl (3-nitrophenyl) phosphate (3e):
Yellow oil; 270 mg (98%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 8.07 (d, J = 6.7 Hz, 2H), 7.62 (d, J = 9.0 Hz, 1H), 7.54 (t, J = 8.5 Hz, 1H), 4.23-4.30 (m. 4H), 1.39 (t, J = 7.4 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 151.1 (d, J = 6.3 Hz), 148.9, 130.3, 126.3 (d, J = 3.6 Hz), 119.8, 115.5 (d, J = 4.5 Hz), 65.0(d, J = 5.4 Hz), 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.6; IR v_{max} cm^{-1}: 2987, 2923, 2378, 1588, 1531, 1477, 1354, 1279, 1224, 1165, 1027, 966, 863, 792, 738, 675, 548; MS (ESI) m/z = 298 (M+Na)$^+$; (ESI-HRMS) calculated for C$_{10}$H$_{14}$O$_6$NNaP (M+Na)$^+$: 298.04509, found: 298.04445.

4-Nitrophenyl diethyl phosphate (3f):
Yellow oil**;** 263 mg (95%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 8.26 (d, J = 9.0 Hz, 2H), 7.41 (d, J= 8.3 Hz, 2H), 4.21-4.31 (m, 4H), 1.38 (t, J = 8.3 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 155.4 (d, J = 5.4 Hz), 144.5, 125.6, 120.4 (d, J = 5.4 Hz), 65.1 (d, J = 6.3 Hz), 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -7.1; IR v_{max} cm^{-1}: 2989, 2914, 2379, 1613, 1592, 1491, 1347, 1278, 1232, 1163, 1099, 1026, 927, 859, 776, 752, 688, 552; MS (ESI) m/z = 276 (M+H)$^+$; (ESI-HRMS) calculated for C$_{10}$H$_{15}$O$_6$NP (M+H)$^+$: 276.06315, found: 276.06259.

4-Carbamoylphenyl diethyl phosphate (3g):
Yellow solid; M.p. 52-55 $^{\circ}$C, 268 mg (98%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.84 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.6, 2H), 6.44 (d, J = 242.5 Hz, 2H), 4.17-4.28 (m, 4H), 1.36 (s, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 168.5, 153.3 (d, J = 7.2 Hz), 130.0, 129.3, 119.8 (d, J = 4.5 Hz), 64.8 (d, J = 5.4 Hz), 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.8; IR v_{max} cm^{-1}: 3377, 3207, 2987, 2378, 1670, 1605, 1509, 1391, 1267, 1166, 1028, 963, 936, 859, 774, 689, 548; MS (ESI) m/z = 274 (M+H)$^+$; (ESI-HRMS) calculated for C$_{11}$H$_{17}$O$_5$NP (M+H)$^+$: 274.08389, found: 274.08336.

2-Bromophenyl diethyl phosphate (3h)
Yellow oil; 295 mg (96%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.93 (d, J = 8.3 Hz, 1H), 7.60 (d, J = 4.8 Hz, 2H), 7.28-7.32 (m, 1H), 4.22-4.32 (m. 4H), 1.37 (t, J = 7.1 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 143.5 (d, J = 5.4 Hz), 143.4, 134.2, 125.3 (d, J = 1.8 Hz), 122.6, 65.4 (d, J = 6.3 Hz), 15.9 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -7.4; IR v_{max} cm^{-1}: 2984, 2910, 2377, 1582, 1475, 1370, 1281, 1232, 1164, 1098, 1027, 932, 759, 653, 547; MS (ESI) m/z = 331 (M+Na)$^+$; (ESI-HRMS) calculated for C$_{10}$H$_{14}$O$_6$NNaP (M+Na)$^+$: 330.97053, found: 330.97003.

4-Chloro-3,5-dimethylphenyl diethyl phosphate (3i):
Yellow oil; 214 mg (73%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 6.96 (s, 2H), 4.17-4.25 (m, 4H), 2.35 (s, 6H), 1.36 (t, J = 7.0 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 148.2 (d, J = 6.3 Hz), 137.6, 130.6, 119.6 (d, J = 5.4 Hz), 64.6 (d, J = 6.3 Hz), 20.7, 16.0 (d, J = 6.3 Hz);. ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.2; IR v_{max} cm^{-1}: 2989, 2913, 2377, 1590, 1469, 1304, 1276, 1155, 1025, 979, 859, 803, 754, 702, 644, 560; MS (ESI) m/z = 315 (M+Na)$^+$; (ESI-HRMS) calculated for C$_{12}$H$_{18}$O$_4$ClNaP (M+Na)$^+$: 315.05234, found: 315.05184.

Methyl 2-((diethoxyphosphoryl)oxy)-4-methoxybenzoate (3j):
Yellow oil; 245 mg (77%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.88 (d, J = 8.8 Hz, 1H), 6.98 (s, 1H), 6.75 (d, J = 8.8 Hz, 1H), 4.23-4.30 (m. 4H), 3.86 (s, 3H), 3.84 (s, 3H), 1.36 (t, J = 7.0 Hz ,6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 164.9, 163.2, 151.4 (d, J = 7.2 Hz), 133.2, 114.8 (d, J = 6.3 Hz), 110.7, 106.9 (d, J = 1.8 Hz), 64.8 (d, J = 6.3 Hz), 55.6, 51.8, 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -7.2; IR v_{max} cm^{-1}: 2978, 1726, 1611, 1505, 1437, 1262, 1195, 1093, 1028, 984, 958, 875, 773, 548; MS (ESI) m/z = 319 (M+H)$^+$; ((ESI-HRMS) calculated for (M+H)$^+$: C$_{13}$H$_{20}$O$_7$P (M+H)$^+$: 319.09412, found: 319.09322.

Diethyl phenyl phosphate (3k):
Yellow oil; 164 mg (71%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.33 (t, J = 8.1 Hz, 2H), 7.20 (q, J = 8.6 Hz, 3H), 4.16-4.27 (m, 4H), 1.35 (t, J = 7.1 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 150.7, 129.6, 124.9, 119.9 (d, J = 4.5 Hz), 64.5 (d, J = 6.3 Hz), 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.3; IR v_{max} cm^{-1}: 2985, 2937, 2377, 1594, 1490, 1369, 1274, 1212, 1164, 1025, 936, 763, 691, 538; MS (ESI) m/z = 253 (M+Na)$^+$; (ESI-HRMS) calculated for C$_{10}$H$_{15}$O$_4$NaP (M+Na)$^+$: 253.06002, found: 253.05977.

Diethyl *m*-tolyl phosphate (3l):
Red oil; 110 mg (45%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.21 (t, J = 7.7 Hz, 1H), 6.99 (t, J = 7.7 Hz, 3H), 4.16-4.27 (m, 4H), 2.34 (s, 3H), 1.35 (t, J = 6.9 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 150.6 (d, J = 6.3 Hz), 139.8, 129.2, 125.6, 120.5 (d, J = 4.5 Hz), 116.8 (d, J = 4.5 Hz), 64.4 (d, J = 5.4 Hz), 21.2, 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.2; IR v_{max} cm^{-1}: 2982, 2913, 2378, 1610, 1588, 1488, 1273, 1151, 1032, 964, 855, 783, 688, 505; MS (ESI) m/z = 245 (M+H)$^+$; (ESI-HRMS) calculated for C$_{11}$H$_{18}$O$_4$P (M+H)$^+$: 245.09372, found: 245.09292.

Diethyl *p*-tolyl phosphate (3m):
Yellow oil; 97 mg (59%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.11 (q, J = 8.5 Hz, 4H), 4.16-4.24 (m, 4H), 2.31 (s, 3H), 1.34 (t, J = 7.0 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 148.4 (d, J = 7.2 Hz), 134.4, 130.0, 119.6 (d, J = 4.5 Hz), 64.4 (d, J = 6.3 Hz), 20.6, 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.0. IR v_{max} cm^{-1}: 2985, 2907, 2378, 1608, 1508, 1445, 1273, 1217, 1165, 1028, 960, 825, 757, 695, 528; MS (ESI) m/z = 245 (M+H)$^+$; (ESI-HRMS) calculated for C$_{11}$H$_{18}$O$_4$P (M+H)$^+$: 245.09372, found: 245.09288.

Diethyl 4-methoxyphenyl phosphate (3n):
Red oil; 149 mg (57%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.14 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 9.1 Hz, 2H), 4.16-4.24 (m, 4H), 3.78 (s, 3H), 1.34 (t, J = 7.0 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 156.5, 144.2 (d, J= 6.3 Hz), 120.8 (d, J = 3.6 Hz), 114.5, 64.4 (d, J = 6.3 Hz), 55.5, 16.0 (d, J = 7.2 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -5.7. IR v_{max} cm^{-1}:2981, 2921, 2377, 1506, 1443, 1273, 1205, 1165, 1031, 960, 835, 813, 759, 637, 535; MS (ESI) m/z = 261 (M+H)$^+$; (ESI-HRMS) calculated for C$_{11}$H$_{18}$O$_5$P (M+H)$^+$: 261.08864, found: 261.08783.

Diethyl (4-hydroxyphenyl) phosphate (3o):
Yellow oil; 87 mg (35%); ^{1}H NMR δ (400 MHz, CDCl$_3$): 7.90 (brs, 1H), 6.93 (d, J = 8.8 Hz, 2H), 6.65 (d, J = 8.6 Hz, 2H), 4.17-4.25 (m, 4H), 1.36 (t, J = 7.1 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 154.0, 143.1 (d, J = 7.2 Hz), 120.7 (d, J = 3.6 Hz), 116.3, 64.7 (d, J = 6.3 Hz), 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -5.8. IR v_{max} cm^{-1}: 3246, 2921, 2854, 2378, 1601, 1509, 1453, 1249, 1198, 1165, 1029, 967, 837, 769, 573; MS (ESI) m/z = 269 (M+Na)$^+$; (ESI-HRMS) calculated for C$_{10}$H$_{15}$O$_5$NaP (M+Na)$^+$: 269.05493, found: 269.05446.

3-Acetamidophenyl diethyl phosphate (3p):
Red oil; 207 mg (72%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 8.32 (s, 1H), 6.98 (s, 1H), 7.55 (s, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 6.88 (d, J = 9.0 Hz, 1H), 4.19-4.28 (m, 4H), 2.11 (s, 3H), 1.37 (t, J = 7.9 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 168.8, 150.6 (d, J = 6.3 Hz), 139.7, 129.6, 116.1, 114.9 (d, J = 4.5 Hz), 111.4 (d, J = 4.5 Hz), 64.7 (d, J = 6.3 Hz), 24.3, 16.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.5. IR v_{max} cm^{-1}: 3277, 2982, 2939, 2378, 1676, 1550, 1485, 1438, 1371, 1267, 1151, 1026, 983, 878, 784, 687, 523; MS (ESI) m/z = 288 (M+H)$^+$; (ESI-HRMS) calculated for C$_{12}$H$_{19}$O$_5$NP (M+H)$^+$: 288.09954, found: 288.09884.

[1,1'-Biphenyl]-2-yl diethyl phosphate (3q):
Yellow oil; 199 mg (65%); ^{1}H NMR δ (400 MHz, CDCl$_3$): 7.30-7.51 (m, 8H), 7.23 (t, J = 7.4 Hz, 1H), 3.85-4.01 (m, 4H), 1.17 (t, J = 6.9 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 147.6 (d, J = 7.2 Hz), 137.4, 131.5 (d, J = 6.3 Hz), 131.1, 129.4, 128.6, 128.0, 127.3, 125.1, 120.4, 64.3 (d, J = 6.3 Hz), 15.9 (d, J= 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.8; IR v_{max} cm^{-1}:3366, 2985, 2937, 2377, 1504, 1479, 1434, 1277, 1207, 1163, 1099, 1029, 957,935, 789, 734, 701,591,553, 506; MS (ESI) m/z = 329 (M+Na)$^+$; (ESI-HRMS) calculated for C$_{16}$H$_{19}$O$_4$NaP (M+Na)$^+$: 329.09132, found: 329.09077.

4-Bromophenyl dimethyl phosphate (4a):
Yellow oil; 84 mg (30%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.46 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 9.00 Hz, 2H), 3.87 (s, 3H), 3.84 (s, 3H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 149.6 (d, J = 6.3 Hz), 132.7, 121.6 (d, J = 5.4 Hz), 118.0, 55.0 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -4.2; IR v_{max} cm^{-1}: 2954, 2925, 2378, 1582, 1284, 1217, 1040, 1011, 947, 830, 793, 548; MS (ESI) m/z = 303 (M+Na)$^+$; (ESI-HRMS) calculated for C$_8$H$_{10}$O$_4$BrNaP (M+Na)$^+$: 302.93923, found: 302.93895.

4-Bromophenyl diisopropyl phosphate (4b):
Yellow oil; 306 mg (91%): ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.45 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 4.69- 4.79 (m, 2H), 1.37 (d, J = 6.2 Hz, 6H), 1.32 (d, J = 6.2 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 150.0 (d, J = 7.2 Hz), 132.4, 121.8 (d, J = 5.4 Hz), 117.5, 73.6 (d, J = 5.4 Hz), 23.5 (d. J = 4.5 Hz), 23.4 (d, J = 4.5 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -8.0; IR v_{max} cm^{-1}:2981, 2378, 1584, 1485, 1387, 1271, 1218, 1143, 1106, 1003, 930, 833, 775, 547; MS (ESI) m/z = 337 (M+H)$^+$; ESI-HRMS) calculated for C$_{12}$H$_{19}$O$_4$BrP (M+H)$^+$: 337.01988, found: 337.01919.

4-Bromophenyl dibutyl phosphate (4c):
Light yellow oil; 281 mg (77%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.45 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 4.11-4.17 (m, 4H), 1.64-1.69 (m, 4H), 1.35-1.43 (m, 4H), 0.92 (t, J = 7.3 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 149.8 (d, J = 6.3 Hz), 132.6, 121.7 (d, J = 4.5 Hz), 117.7, 68.3 (d, J = 5.4 Hz), 32.1 (d, J = 6.3 Hz), 18.5, 13.4; ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.2; IR v_{max} cm^{-1}: 2960, 2931, 2872, 2378, 1583, 1485, 1284, 1217, 1165, 1066, 1026, 1011, 943, 930, 832, 756, 633, 548; MS (ESI) m/z = 387 (M+Na)$^+$; (ESI-HRMS) calculated for C$_{12}$H$_{22}$O$_4$BrNaP (M+Na)$^+$: 387.03313, found: 387.03339.

3-Chlorophenyl diisopropyl phosphate (4d):
Yellow oil; 234 mg (80%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.26 (t, J = 5.7 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.72-4.78 (m, 2H), 1.38 (d, J = 6.2 Hz, 6H), 1.33 (d, J = 6.1 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 151.3 (d, J = 7.2 Hz), 134.7, 130.2, 125.6, 120.6 (d, J = 5.4 Hz), 118.3 (d, J = 4.5 Hz), 73.7 (d, J = 6.3 Hz), 23.6 (d, J = 4.5 Hz), 23.5 (d, J = 4.5 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -8.2; IR v_{max} cm^{-1}: 2982, 2937, 2377, 1589, 1472, 1387, 1179, 1143, 1272, 1247, 1003, 950, 815, 780, 678, 527; MS (ESI) m/z = 293 (M+H)$^+$; (ESI-HRMS) calculated for C$_{12}$H$_{19}$O$_4$ClP (M+H)$^+$: 293.07040, found: 293.06968.

Methyl 2-(diisopropoxyphosphoryloxy)-4-methoxybenzoate (4e):
Yellow oil; 284 mg (82%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.87 (d, J = 8.8 Hz, 1H), 7.03 (s, 1H), 6.74 (d, J = 8.6 Hz, 1H), 4.78- 4.85 (m, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 1.37 (d, J = 6.2 Hz, 6H), 1.32(d, J = 6.2 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 165.1, 163.4, 151.5 (d, J = 7.2 Hz), 133.1, 115.0 (d, J = 6.3 Hz), 110.8, 73.6 (d, J = 6.3 Hz), 55.5, 51.7, 23.6 (d, J = 4.5 Hz), 23.4 (d, J = 5.4 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -8.9; IR v_{max} cm^{-1}: 2982, 2378, 1728, 1610, 1577, 1507, 1436, 1262, 1197, 1142, 1091, 1008, 893, 868, 773, 698, 519'; MS (ESI) m/**z** = 347 (M+H)$^+$; (ESI-HRMS) calculated for C$_{15}$H$_{24}$O$_7$P (M+H)$^+$: 347.12542, found: 347.12368.

Dibutyl 4-chloro-3,5-dimethylphenyl phosphate (4f):
Yellow oil; 286 mg (82%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 6.95 (s, 2H), 4.10-4.16 (m, 4H), 2.35 (s, 6H), 1.64-1.70 (m, 4H), 1.36-1.44 (m, 4H), 0.91-0.94 (t, J = 7.4 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 148.3 (d, J = 7.2 Hz), 137.6,130.6, 119.7 (d, J = 4.5 Hz), 68.2 (d, J = 6.3 Hz), 32.1 (d, J = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.0; IR v_{max} cm^{-1}: 3364, 2962, 2872, 2377, 1748, 1591, 1548, 1470, 1286, 1155, 1027, 979, 879, 640, 559; MS (ESI) m/z = 349 (M+H)$^+$; (ESI-HRMS) calculated for C$_{16}$H$_{27}$O$_4$ClP (M+H)$^+$: 349.13300, found: 349.13238.

Dibutyl (2-nitrophenyl) phosphate (4g):
Yellow oil; 298 mg (90%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.94 (d, J = 7.7 Hz, 1H), 7.55-764 (m, 2H), 7.28-7.32 (m, 1H), 4.16-4.26 (m, 4H), 1.73-1.66 (m, 4H), 1.34-1.46 (m, 4H), 0.92 (t, J = 7.3 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 143.5 (d, J = 5.4 Hz), 141.4 (d, J = 6.3 Hz), 134.2, 125.5, 125.0, 122.5, 69.0 (d, J = 6.3Hz) 32.0 (d, J = 7.2 Hz), 18.4, 13.4; ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -7.2; IR v_{max} cm^{-1}: 2962, 2940, 2874, 2378, 1604, 1532, 1289, 1235, 1149, 1029, 932, 848, 780, 743, 657, 547, 522; MS (ESI) m/z = 332 (M+H)$^+$; (ESI-HRMS) calculated for C$_{14}$H$_{22}$O$_6$NP (M+H)$^+$: 332.12575 found: 332.12564.

2-Nitrophenyl diphenyl phosphate (4h):
Yellow oil; 38 mg (10%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.96 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 6.2 Hz, 2H), 7.30-7.39 (m, 6H), 7.20-7.27 (m, 5H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 150.1 (d, J = 8.1 Hz), 143.0 (d, J = 5.4 Hz), 134.3, 129.9, 125.9, 125.8 (d, J = 7.2 Hz), 122.5, 120.0 (d, J = 5.4 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -18.5; IR v_{max} cm^{-1}:2925, 2855, 2377, 1590, 1532, 1486, 1351, 1302, 1351, 1302, 1270, 1184, 1161, 1089, 1010, 954, 849, 688, 656, 581, 503; MS (ESI) m/z =372 (M+H)$^+$; (ESI-HRMS) calculated for C$_{18}$H$_{15}$O$_6$NP (M+H)$^+$: 372.06315, found: 372.06308.

2-Nitrophenyl diphenylphosphinate (4i):
Yellow oil; 99 mg (29%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.97 (q, J = 8.3 Hz, 4H), 7.85 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.55 (t, J = 7.4 Hz, 2H), 7.45-7.49 (m, 5H), 7.18 (t, J = 8.0 Hz, 1H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 144.2 (d, J = 8.1 Hz), 134.3, 132.9, 131.7 (d, J = 10.8 Hz), 130.2, 129.1, 128.8 (d, J = 13.6 Hz), 125.7, 124.5, 122.9 (d, J = 3.6 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ 33.7; IR v_{max} cm^{-1}:3245, 3055, 2923,

2850, 2377, 2310, 1729, 1603, 1528, 1483, 1438, 1351, 1271, 1228, 1130, 1089, 1033, 997, 956, 913, 844, 730, 695, 59, 527; MS (ESI) m/z = 340 (M+H)$^+$; (ESI-HRMS) calculated for $C_{18}H_{15}O_4NP$ (M+H)$^+$:340.07332 found: 340.07252.

4-bromophenyl ethyl phenylphosphonate (4j):
Yellow oil; 153 mg (45%); ^{1}H NMR δ (300 MHz, $CDCl_3$): 7.86 (q, *J* = 6.8 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.44-7.51(m, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 4.19-4.30 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR δ (100 MHz, $CDCl_3$): 149.6 (d, *J* = 7.1 Hz), 132.9, 132.5, 131.9 (d, *J* = 10.1 Hz), 128.5 (d, *J* = 15.2 Hz), 128.1, 126.2, 122.3 (d, *J* = 4.0 Hz), 117.7, 63.0 (d, *J* = 6.1 Hz), 16.2 (d, *J* = 6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm): ŭ 15.7; IR v_{max} cm^{-1}: 3482, 2985, 1634, 1482, 1259, 1213, 1131, 1035, 919, 832, 754, 551; MS (ESI) m/z = 341 (M+H)$^+$; HRMS m/z (ESI) calculated for $C_{14}H_{15}O_3BrP$ (M+H)$^+$: 340.99367, found: 340.99227.

Diisopropyl m-tolyl phosphate (4k):
Yellow oil; 83 mg (30%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 7.19 (t, *J* = 7.9 Hz, 1H),7.02 (t, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.70-4.78 (m, 2H), 2.33 (s, 3H), 1.37 (d, *J* = 6.1 Hz, 6H), 1.31 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 150.8 (d, *J* = 7.2 Hz), 139.7, 129.1, 125.4, 120.6 (d, *J* = 5.4 Hz), 116.9 (d, *J* = 5.4 Hz), 73.3 (d, *J* = 5.4 Hz), 23.6 (d, *J* = 4.5 Hz), 23.5 (d, *J* = 4.5 Hz), 21.2; ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ŭ -7.9; IR v_{max} cm^{-1}: 2981, 2937, 2377, 1610, 1588, 1488, 1386, 1271, 1252, 1149, 1107, 997, 961, 893, 848, 783, 688, 537; MS (ESI) m/z = 295 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{13}H_{21}O_4NaP$ (M+Na)$^+$: 295.10697, found: 295.10613.

Diisopropyl 4-methoxyphenyl phosphate (4l):
Yellow oil; 131 mg (45%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 7.14 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 2H), 4.69-4.77 (m, 2H), 3.77 (s, 3H), 1.36 (d, *J* = 6.1 Hz, 6H), 1.30 (d, *J* = 6.2 Hz, 6H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 156.4, 144.5 (d, *J* = 7.2 Hz), 120.9 (d, *J* = 4.5 Hz), 114.4, 73.2 (d, *J* = 5.4 Hz), 65.5, 23.6 (d, *J* = 4.5 Hz), 23.5 (d, *J* = 4.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ŭ -7.4; IR v_{max} cm^{-1}: 2981, 2937, 2378, 1506, 1387, 1250, 1206, 1179, 1105, 1001, 942, 810, 834, 810, 636, 535; MS (ESI) m/z = 311 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{13}H_{21}O_5NaP$ (M+Na)$^+$: 311.10188, found: 311.10108.

O-4-cyanophenyl O,O-dimethyl phosphorothioate (4m):
Yellow oil; 106 mg (43%). ^{1}H NMR δ (500 MHz, $CDCl_3$): 7.68 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 3.89 (s, 3H), 3.85 (s, 3H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 153.7 (d, *J* = 7.2 Hz), 133.8, 121.8 (d, *J* = 4.5 Hz), 118.1, 109.2, 55.3 (d, *J* = 5.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ŭ 65.7; IR v_{max} cm^{-1}:2953, 2850, 2374, 2230, 1602, 1500, 1228, 1169, 1031, 923, 834, 797, 687, 551; MS (ESI) m/z = 244 (M+H)$^+$; (ESI-HRMS) calculated for $C_9H_{11}O_3NPS$ (M+H)$^+$: 244.01918, found: 244.01871.

O,O-dimethyl O-4-nitrophenyl phosphorothioate (4n):
Yellow oil; 153 mg (58%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 8.26 (d, *J* = 9.15 Hz, 2H), 7.34 (d, *J* = 9.15 Hz, 2H), 3.90 (s, 3H), 3.87 (s, 3H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 155.23-155.29 (d, *J* = 7.2 Hz), 144.8, 125.4, 121.4-121.5 (d, *J* = 5.4 Hz), 55.42-55.46 (d, *J* = 5.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ŭ 65.6; IR v_{max} cm^{-1}: 2953, 2377, 2309, 1613, 1590, 1490, 1347, 1225, 1111, 1031, 924, 859, 766, 646, 503; MS (ESI) m/z = 264 (M+H)$^+$.

O-3-(3-hydroxyphenylthio)phenyl O,O-dimethyl phosphorothioate (4o):
Yellow oil; 40 mg (11%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 7.36 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 3.81 (s, 3H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 156.0, 148.8 (d, *J* = 8.1 Hz), 135.4, 135.1, 129.5, 124.3, 121.3 (d, *J* = 4.5 Hz), 116.5, 55.1 (d, *J* = 5.4 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ŭ 66.5. IR v_{max} cm^{-1}: 3388, 2951, 2846, 2377, 1598, 1583, 1486, 1265, 1208, 1165, 1032, 943, 927, 827, 777, 656, 535, 516; MS (ESI) m/z = 343 (M+H)$^+$; (ESI-HRMS) calculated for $C_{14}H_{16}O_4PS_2$ (M+H)$^+$: 343.02221, found: 343.02194.

Diethyl naphthalen-2-yl phosphate (5a):
Red oil; 140 mg (50%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 7.81 (t, *J* = 8.8 Hz, 3H), 7.68 (s, 1H), 7.42-7.50 (m, 2H), 7.37 (d, *J* = 9.0 Hz, 1H), 4.21-4.29 (m, 4H), 1.36 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 148.3 (d, *J* = 6.3 Hz), 133.8, 130.8, 129.7, 127.6, 127.4, 126.6, 125.4, 119 (d, *J* = 4.5 Hz), 116.3 (d, *J* = 4.5 Hz), 64.6 (d, *J* = 5.4 Hz), 16.1 (d, *J* = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ŭ -6.2. IR v_{max} cm^{-1}: 2983, 2931, 2377, 1632, 1598, 1510, 1465, 1358, 1277, 1247, 1213, 1162, 1028, 972, 865, 814, 751, 687, 559, 478; MS (ESI) m/z = 303 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{14}H_{17}O_4NaP$ (M+Na)$^+$: 303.07567, found: 303.07523.

1-Bromonaphthalen-2-yl diethyl phosphate (5b):
Red oil; 330 mg (92%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 8.27 (d, *J* = 9.0 Hz, 1H), 7.81 (t, *J* = 9.6 Hz, 2H), 7.61-7.67 (m, 2H), 7.51 (t, *J* = 7.93 Hz, 1H) 4.28-4.36 (m, 4H), 1.38 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 146.0, 132.7, 131.5, 128.9, 128.1,127.8, 126.9, 125.9, 119.8, 112.8 (d, *J* = 8.8 Hz), 65.0 (d, *J* = 6.0 Hz), 16.0 (d, *J* = 6.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ŭ -6.8; IR v_{max} cm^{-1}: 2986, 2907, 2377, 1624, 1597, 1501, 1356, 1283, 1254, 1231, 1165, 1029, 999, 964, 848, 811, 749, 637, 522; MS (ESI) m/z = 381 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{14}H_{16}O_4BrNaP$ (M+Na)$^+$: 380.98618, found: 380.98612.

6-Bromonaphthalen-2-yl diethyl phosphate (5c):
Yellow oil; 297 mg (83%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 7.98 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.39 (d. *J* = 9.0 Hz, 1H), 4.21-4.29 (m, 4H), 1.36 (t, J = 7.1 Hz, 6H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 148.5 (d, *J* = 7.2 Hz), 132.2, 131.8, 130.0, 129.6, 129.0, 128.8, 121.0 (d, *J* = 5.4 Hz), 119.2, 116.3 (d, *J* = 5.4 Hz), 64.7 (d, *J* = 6.3 Hz), 16.0 (d, *J* = 6.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ŭ -6.3; IR v_{max} cm^{-1}: 2984, 2937, 2377, 1628, 1589, 1500, 1363, 1276, 1246, 1198, 1150, 1054, 1028, 975, 934, 880, 801, 755, 705, 648, 575, 504; MS (ESI) m/z = 381 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{14}H_{16}O_4BrNaP$ (M+Na)$^+$: 380.98618, found: 380.98593.

6-Bromonaphthalen-2-yl diisopropyl phosphate (5d):
Yellow oil; 247 mg (64%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 7.98 (s, 1H), 7.65- 7.74 (m, 3H), 7.56 (d, *J* = 8.8 Hz, 1H), 7.40 (d, *J* = 9.06 Hz, 1H), 4.73-4.86 (m, 2H), 1.39 (d, *J* = 6.0 Hz, 6H), 1.33 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 148.8 (d, *J* = 7.2 Hz), 132.2, 131.7, 129.9, 129.6, 129.0, 128.7, 121.2 (d, *J* = 4.5 Hz), 119.1, 116.4 (d, *J* = 4.5 Hz), 73.6 (d, *J* = 6.3 Hz), 23.6 (d, *J* = 4.5 Hz), 23.5 (d, *J* = 4.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ŭ -8.2; IR v_{max} cm^{-1}: 3010, 2979, 2910, 2378, 2313, 1589, 1500, 1272, 1247, 1199, 1003, 972, 935, 879, 785, 645, 520; MS (ESI) m/z = 387 (M+H)$^+$; (ESI-HRMS) calculated for $C_{16}H_{21}O_4BrP$ (M+H)$^+$: 387.03553, found: 387.03511.

Diethyl (7-methoxynaphthalen-2-yl) phosphate (5e):
Red oil; 177 mg (57%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 7.72 (q, *J* = 8.8 Hz, 2H), 7.59 (s, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 7.10 (t, *J* = 7.1 Hz, 2H), 4.21-4.29 (m, 4H), 3.91 (s, 3H), 1.36 (t, *J* = 5.3 Hz, 6H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 158.2, 148.9 (d, *J* = 7.2 Hz), 135.2, 129.4, 129.1, 126.2, 118.3, 117.4 (d, *J* = 5.4 Hz), 115.3 (d, *J* = 5.4 Hz), 105.4, 64.6 (d, *J* = 6.3 Hz), 55.2, 16.0 (d, *J* = 6.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ŭ -6.2; IR v_{max} cm^{-1}: 2983, 2925, 2378, 1632, 1513, 1467, 1390, 1252, 1216, 1153, 1029, 983, 911, 853, 774, 545; MS (ESI) m/z = 333 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{15}H_{19}O_5NaP$ (M+Na)$^+$: 333.08623, found: 333.08595.

***rac*-Diethyl (2'-hydroxy-[1,1'-binaphthalen]-2-yl) phosphate (5f):**
White solid; M.p. 92-97 °C, 51 mg (12%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 8.03 (d, *J* = 8.8 Hz, 1H), 7.82-7.94 (m, 3H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.46 (t, *J* = 6.7 Hz, 1H), 7.20-7.39 (m, 5H), 7.04 (d, *J* = 8.3 Hz, 1H), 3.87-3.97 (m, 2H), 3.48-3.61 (m, 1H), 3.26-3.40 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 152.2, 147.2,

147.2, 133.6, 131.5, 130.7, 130.0, 129.1, 128.1, 127.8, 127.4, 126.5, 125.9, 125.7, 124.6, 123.5, 122.6, 122.5, 119.8, 119.5, 115.8, 64.8, 64.7, 64.3, 64.3, 15.8, 15.8, 15.4, 15.4; ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -5.1; IR v_{max} cm^{-1}:3230, 2979, 2929, 2374, 1620, 1595, 1474, 1253, 1222, 1144, 1032, 1000, 869, 818, 748, 623; MS (ESI) m/z = 423 (M+H)$^+$; ESI-HRMS) calculated for $C_{24}H_{24}O_5P$ (M+H)$^+$: 423.13559, found: 423.13497.

***rac*-[1,1'-binaphthalene]-2,2'-diyl tetraethyl bis(phosphate) (5fa):**
white solid; M.p. 142-147 °C, 224 mg (40%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.98 (d, J = 9.0 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.27-7.33 (m, 4H), 3.67-3.76 (m, 4H), 3.46-3.52 (m, 4H), 1.06 (t, *J* = 7.0 Hz, 6H), 0.84 (t, *J*= 7.0 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 146.6 (d, *J* = 6.358 Hz),133.4, 130.7, 129.9, 127.8, 126.9, 126.1, 125.3, 121.5 (d, *J* = 8.1 Hz), 119.1, 64.3 (d, *J* = 6.3 Hz), 64.0 (d, J = 6.3 Hz), 15.7 (d, *J* = 6.3 Hz), 15.5 (d, *J* = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -7.5; IR v_{max} cm^{-1}:2980, 2922, 2378, 1624, 1592, 1508, 1475, 1362, 1278, 1226, 1164, 1100, 1028, 997, 845, 815, 751, 699, 500; MS (ESI) m/z = 581 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{28}H_{32}O_8NaP_2$ (M+Na)$^+$: 581.14646, found: 581.14537.

***R*-Diethyl (2'-hydroxy-[1,1'-binaphthalen]-2-yl) phosphate (5g):**
White solid; M.p. 165-167 °C, 51 mg (12%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 8.05 (d, *J* = 9.0 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.64(d, *J* = 9.0 Hz, 1H). 7.48(t, *J* = 7.0 Hz, 1H), 7.41(d, *J* = 8.8 Hz, 1H), 7.34(q, *J* = 6.1 Hz, 2H), 7.23-7.27 (m, 2H), 7.05 (d, *J* = 8.2 Hz, 1H), 3.92-3.97 (m, 2H), 3.53-3.61 (m, 1H), 3.31-3.39 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR δ (125 MHz, CDCl$_3$): 152.1, 147.2(d, *J* = 7.2 Hz), 133.7, 131.6, 130.8, 130.0, 129.1, 128.1, 127.8, 127.4, 126.6, 125.9, 125.7, 124.6, 123.6, 122.5, 119.8, 119.6, 116.0, 64.7 (d, *J* = 6.3 Hz), 64.3 (d, *J* = 6.3 Hz), 15.8 (d, *J* = 7.2 Hz), 15.4 (d, *J* = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -5.0; IR v_{max} cm^{-1}: 3051, 2928, 2855, 2346, 1623, 1507, 1434, 1249, 1211, 1060, 1019, 989, 976, 869, 816, 748, 600, 519 MS (ESI) m/z = 445 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{24}H_{23}O_5NaP$ (M+Na)$^+$: 445.11753, found: 445.11410.

***R*-[1,1'-binaphthalene]-2,2'-diyl tetraethyl bis(phosphate) (5ga):**
White solid; M.p. 52-55 °C, 129 mg (23%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.98 (d, *J* = 9.0 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.27-7.34 (m, 4H), 3.65-3.77 (m, 4H), 3.46-3.52 (m, 4H), 1.06 (t, *J* = 7.0 Hz, 6H), 0.84 (t, *J*= 7.0 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 146.6 (d, *J* = 6.6 Hz),133.4, 130.7, 129.9, 127.8, 126.9, 126.1, 125.3, 121.5 (d, *J* = 8.1 Hz), 119.1, 64.3 (d, *J* = 6.3 Hz), 64.0 (d, *J* = 6.3 Hz), 15.7 (d, *J* = 6.3 Hz), 15.3 (d, *J* = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -7.5; IR v_{max} cm^{-1}: 2983, 2922, 2377, 1623, 1592, 1507, 1474, 1361, 1277, 1225, 1164, 1100, 1027, 997, 845, 819, 750, 700, 583, 526; MS (ESI) m/z = 559 (M+H)$^+$; (ESI-HRMS) calculated for $C_{28}H_{33}O_8P_2$ (M+H)$^+$: 559.16452, found: 559.16348.

S-Diethyl (2'-hydroxy-[1,1'-binaphthalen]-2-yl) phosphate (5h):
White solid; M.p. 142-147 °C, 51 mg (12%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 8.05 (d, *J* = 9.0 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.64(d, *J* = 9.0 Hz, 1H). 7.48(t, *J* = 7.9 Hz, 1H), 7.41(d, *J* = 8.8 Hz, 1H), 7.34(q, *J* = 8.3 Hz, 2H), 7.23-7.28 (m, 3H), 7.05 (d, *J* = 8.5 Hz, 1H), 3.92-3.98 (m, 2H), 3.53-3.61 (m, 1H), 3.31-3.39 (m, 1H), 1.21 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR δ (125 MHz, CDCl$_3$): 152.1, 147.2(d, *J* = 7.2 Hz, 133.7, 131.6, 130.8, 130.0, 129.1, 128.1, 127.8, 127.4, 126.6, 125.9, 125.7, 124.6, 123.6, 122.5, 119.8, 119.6, 116.0, 64.7 (d, J = 6.3 Hz), 64.3 (d, *J* = 6.3 Hz), 15.8 (d, *J* = 7.2 Hz), 15.4 (d, *J* = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ ï 5.0; IR v_{max} cm^{-1}: 3051, 2981, 2929, 2350, 1623, 1593, 1507, 1434, 1249, 1220, 1029, 990, 869, 816, 749, 702, 554; MS (ESI) m/z = 423 (M+H)$^+$; (ESI-HRMS) calculated for $C_{24}H_{24}O_5P$ (M+H)$^+$: 423.13559, found: 423.13579.

***S*-[1,1'-binaphthalene]-2,2'-diyl tetraethyl bis(phosphate) (5ha):**
White solid; M.p. 57-60 °C, 240 mg (43%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.99 (d, *J* = 9.0 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 9.0 Hz, 2H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.27-7.34 (m, 4H), 3.65-3.77 (m, 4H), 3.46-3.52 (m, 4H), 1.06 (t, *J* = 7.0 Hz, 6H), 0.84 (t, *J*= 7.0 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 146.6 (d, J = 5.4 Hz),133.4, 130.7, 129.9, 127.8, 126.9, 126.1, 125.3, 121.5 (d, *J* = 8.1 Hz), 119.1, 64.3 (d, *J* = 6.3 Hz), 64.0 (d, *J* = 6.3 Hz), 15.7 (d, *J* = 6.3 Hz), 15.3 (d, *J* = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -7.5; IR v_{max} cm^{-1}: 2983, 2922, 2377, 1623, 1592, 1507, 1474, 1362, 1278, 1226, 1164, 1100, 1027, 997, 845, 815, 751, 700, 583, 520; MS (ESI) m/z = 559 (M+H)$^+$; (ESI-HRMS) calculated for $C_{28}H_{33}O_8P_2$ (M+H)$^+$: 559.16452, found: 559.16349.

Diethyl 2-oxo-2H-chromen-7-yl phosphate (6a):
White solid; M.p. 62-65 °C, 148 mg (49%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.70 (d, *J* = 9.4 Hz, 1H), 7.48 (d, *J* = 9.2 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 2H), 6.39 (d, *J* = 9.6 Hz, 1H), 4.21-4.31 (m, 4H), 1.38 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 160.2, 154.8, 153.2 (d, *J* = 6.3 Hz), 142.7, 128.9, 1116.7 (d, *J* = 4.5 Hz), 115.9, 115.6, 108.5 (d, *J* = 5.4 Hz), 64.9- (d, *J* = 6.3 Hz), 16.0 (d, *J* = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.8; IR v_{max} cm^{-1}:3566, 2984, 2915, 2377, 1737, 1614, 1564, 1503, 1398, 1272, 1232, 1153, 1124, 1099, 1027, 992, 956, 916, 843, 799, 755, 630, 502; MS (ESI) m/z = 299 (M+H)$^+$; (ESI-HRMS) calculated for $C_{13}H_{16}O_6P$ (M+H)$^+$: 299.06790, found: 299.06702.

Diethyl quinolin-8-yl phosphate (6b):
Black oil; 168 mg (59%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 8.97 (s, 1H), 8.17 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 5.0 Hz, 1H), 7.48-7.52 (m, 1H), 7.43-7.47 (m, 1H), 4.33-4.42 (m, 4H), 1.37 (t, *J* = 7.9 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 150.2, 146.7 (d, *J* = 6.3 Hz), 140.9 (d, *J* = 5.4 Hz), 135.8, 129.6, 126.2, 124.5, 121.7, 119.2 (d, *J* = 2.7 Hz), 64.7 (d, J = 5.4 Hz), 16.0 (d, *J* = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.0; IR v_{max} cm^{-1}:3419, 2982, 2378, 1500, 1472, 1370, 1273, 1164, 1096, 1027, 964, 927, 833, 793, 543; MS (ESI) m/z = 282 (M+H)$^+$; (ESI-HRMS) calculated for $C_{13}H_{17}O_4NP$ (M+H)$^+$: 282.08897, found: 282.08758.

Diethyl 2-methylquinolin-8-yl phosphate (6c):
Yellow oil; 197 mg (66%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 8.04 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 5.9 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 4.38 -4.46 (m, 4H), 2.74 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 159.0, 146.3 (d, *J* = 7.2 Hz), 140.5 (d, *J* = 4.5 Hz), 135.8, 127.9, 125.2, 124.4, 122.6, 119.5 (d, *J* = 2.7 Hz), 64.7 (d, *J* = 5.4 Hz), 25.4, 16.0 (d, *J* = 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.0; IR v_{max} cm^{-1}:2982, 2914, 2377, 1603, 1503, 1432, 1251, 1231, 1166, 1095, 1028, 957, 933, 884, 839, 760, 502; MS (ESI) m/z = 318 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{14}H_{18}O_4NNaP$ (M+Na)$^+$: 318.08657, found: 318.08549.

2-(2H-benzo[d][1,2,3]triazol-2-yl)-4-methylphenyl diethyl phosphate (6d):
Yellow oil; 273 mg (75%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.94 (q, *J* = 3.2 Hz, 2H), 7.67 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 6.7 Hz, 2H), 7.32 (d, *J* = 6.7 Hz, 1H), 4.00-4.11 (m, 4H), 2.43 (s, 3H), 1.18 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR δ (125 MHz, CDCl$_3$): 144.8, 141.7 (d, *J* = 6.3 Hz), 135.4, 131.8(d, *J* = 6.3 Hz), 131.3, 127.3, 127.0, 121.7, 118.2, 64.7(d, *J* = 6.3 Hz), 20.6, 15.8 (d, *J*= 6.3 Hz); ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -6.9; IR v_{max} cm^{-1}:2983, 2925, 2377, 1563, 1511, 1277, 1233, 1164, 1029, 932, 882, 823, 749, 580; MS (ESI) m/z = 362 (M+H)$^+$; (ESI-HRMS) calculated for $C_{17}H_{21}O_4N_3P$ (M+H)$^+$: 362.12642, found: 362.12553.

2-(1H-benzo[d]imidazol-2-yl)phenyl diethyl phosphate (6e):
Yellow oil; 214 mg (61%); ^{1}H NMR δ (500 MHz, CDCl$_3$): 8.33 (d, *J* = 7.4 Hz, 1H), 7.69 (s, 2H), 7.28-7.47 (m, 5H), 4.16-4.33 (m, 4H), 1.33 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR δ (75 MHz, CDCl$_3$): 148.1, 147.5 (d, *J* = 7.2 Hz), 131.6, 131.0, 126.0, 122.8, 122.3 (d, *J* = 6.3 Hz), 121.2, 65.4(d, J = 6.6 Hz), 16.0 (d, *J* = 7.2 Hz). ^{31}P NMR (202 MHz, CDCl$_3$, ppm): ŭ -5.2; IR v_{max} cm^{-1}:2979, 2377, 1627, 1489, 1454, 1274, 1215, 1163, 1031, 964,

932, 746, 616, 521; MS (ESI) m/z = 347 (M+H)$^+$; (ESI-HRMS) calculated for $C_{17}H_{20}O_4N_2P$ (M+H)$^+$: 347.11552, found: 347.11493.

2-(Benzo[d]thiazol-2-yl)phenyl diethyl phosphate (6f):
Red oil; 227 mg (62%); ^{1}H NMR δ (400 MHz, $CDCl_3$): 8.44 (d, *J* = 7.8 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.95(d, *J* = 7.9 Hz, 1H), 7.66(d, *J* = 8.3 Hz, 1H), 7.44-7.52 (m, 2H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H) 4.21-4.30 (m, 4H), 1.32 (t, *J* = 7.8 Hz, 6H); ^{13}C NMR δ (125 MHz, $CDCl_3$): 162.1, 152.3, 148.6 (d, *J* = 6.3 Hz), 135.9, 131.6, 130.2, 126.1, 125.0(d, *J* = 10.8 Hz), 124.6(d, *J* = 8.1 Hz), 123.1, 121.4, 119.8, 65.0(d, *J* = 5.4 Hz), 16.0(d, *J*= 6.3 Hz). ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ǔ -6.9; IR v_{max} cm^{-1}: 3065, 2983, 1580, 1285, 1210, 1162, 1026, 974, 857, 759, 730, 691, 517; MS (ESI) m/z = 364 (M+H)$^+$; (ESI-HRMS) calculated for (M+H)$^+$: $C_{17}H_{19}O_4NPS$ (M+H)$^+$: 364.07669, found: 364.07510.

Diethyl methylphosphate (8a):
Colorless liquid; 138 mg (65%); ^{1}H NMR δ (300 MHz, $CDCl_3$): 4.08-4.18 (m, 4H), 3.78 (d, *J* = 11.0 Hz, 3H), 1.36 (t, *J* = 6.8 Hz, 6H); ^{13}C NMR δ (100 MHz, $CDCl_3$): 63.7 (d, *J* = 6.1 Hz), 54.0 (d, *J*= 6.1 Hz), 16.0 (d, *J* = 6.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm): ǔ 0.1; IR v_{max} cm^{-1}: 3451, 2988, 1643, 1259, 1032; MS (ESI) m/z = 169 (M+H)$^+$; HRMS m/z (ESI) calculated for $C_5H_{14}O_4P$ (M+H)$^+$: 169.06242, found: 169.06153.

Triethyl phosphate (8b):
Colorless liquid; 137 mg (65%); ^{1}H NMR δ (400 MHz, $CDCl_3$): 4.07-4.15 (m, 6H), 1.34 (t, *J* = 8.4 Hz, 9H); ^{13}C NMR δ (100 MHz, $CDCl_3$): 63.4 (d, *J* = 6.5 Hz), 16.0 (d, *J* = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm): ǔ -6.47; IR v_{max} cm^{-1}: 3455, 2980, 1642, 1259, 1031; MS (ESI) m/z = 183 (M+H)$^+$; HRMS m/z (ESI) calculated for $C_6H_{16}O_4P$ (M+H)$^+$: 183.07807, found: 183.07706.

Diethyl propylphoshate (8c):
Colorless liquid; 147 mg (65%); ^{1}H NMR δ (400 MHz, $CDCl_3$): 4.07-4.15 (m, 4H), 3.99 (q, *J* = 10.8 Hz, 2H) 1.66-1.75 (m, 2H), 1.34 (t, *J* = 7.5 Hz, 6H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR δ (100 MHz, $CDCl_3$): 69.1 (d, *J* = 6.1 Hz), 63.6 (d, *J*= 6.1 Hz), 23.6 (d, *J*= 6.9 Hz), 16.0 (d, *J* = 6.9 Hz), 9.9; ^{31}P NMR (162 MHz, $CDCl_3$, ppm): ǔ -0.8; IR v_{max} cm^{-1}: 3457, 2978, 1641, 1260, 1029; MS (ESI) m/z = 197 (M+H)$^+$; HRMS m/z (ESI) calculated for $C_7H_{18}O_4P$ (M+H)$^+$: 197.09372, found: 197.09265.

Decyl diethyl phosphate (8d):
Yellow oil; 54 mg (15%); ^{1}H NMR δ (500 MHz, $CDCl_3$): 3.99-4.16 (m, 6H), 1.82 (s, 2H), 1.63-1.71 (m, 2H), 1.26-1.36 (m, 18H), 0.88 (t, *J* = 6.0 Hz,3H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 67.6 (d, *J* = 5.4 Hz), 63.5 (d, *J* = 5.4 Hz), 31.8, 30.2 (d, *J* = 7.2 Hz), 29.4, 29.2, 29.1, 25.4, 22.6, 16.1 (d, *J* = 6.3 Hz), 14.0; ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ǔ -0.8; IR v_{max} cm^{-1}: 2924, 2855, 2378, 1508, 1459, 1394, 1264, 1166, 1031, 976; MS (ESI) m/z = 317 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{14}H_{31}O_4NaP$ (M+Na)$^+$: 317.18522, found: 317.18463.

Diethyl (3-phenylprop-2-yn-1-yl) phosphate (8e):
Yellow oil; 54 mg (20%); ^{1}H NMR δ (400 MHz, $CDCl_3$): 7.43-7.46 (m, 2H), 7.29-7.37 (m, 3H), 4.90 (d, *J* = 10.0 Hz, 2H), 4.14-4.21 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR δ (75 MHz, $CDCl_3$): 131.7, 128.8, 121.9, 87.2, 82.9 (d, *J* = 7.2 Hz), 64.0 (d, *J* = 5.4 Hz), 55.7 (d, *J* = 5.4 Hz), 16.0 (d, *J* = 7.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$, ppm): ǔ -0.9; IR v_{max} cm^{-1}: 2981, 2924, 2854, 2377, 1490, 1373, 1266, 1165, 1023, 970, 836, 751, 691, 546; MS (ESI) m/z = 291 (M+Na)$^+$; (ESI-HRMS) calculated for $C_{13}H_{17}O_4NaP$ (M+Na)$^+$: 291.07567, found: 291.07503.

diethyl benzylphosphoramidate (8f):
Orange liquid; 158 mg (65%); ^{1}H NMR δ (400 MHz, $CDCl_3$): 7.24-7.36 (m, 5H), 3.97-4.13 (m, 6H), 3.05 (brs, 1H),1.30 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR δ (125 MHz, $CDCl_3$): 139.5 (d, *J* = 6.6 Hz), 128.5, 127.2 (d, *J* = 10.4 Hz), 62.6 (d, *J*= 4.7 Hz), 45.3, 16.1 (d, *J* = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm): ǔ 8.4; IR v_{max} cm^{-1}: 3417, 2982, 2908, 1641, 1449, 1231, 1031, 964, 868; MS (ESI) m/z = 244 (M+H)$^+$; HRMS m/z (ESI) calculated for $C_{11}H_{19}O_3NP$ (M+H)$^+$: 244.10971, found: 244.10834.

Diethyl 4-chlorophenylphosphoramidate (8g):
Brown solid; M.p. 70-72 °C, 82 mg (65%); ^{1}H NMR δ (400 MHz, $CDCl_3$): 7.18 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.02-4.21 (m, 4H), 1.31 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR δ (100 MHz, $CDCl_3$): 138.6, 129.1, 126.3, 118.4 (d, *J* = 7.6 Hz), 62.7 (d, *J* = 4.3 Hz), 16.0 (d, *J* = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, ppm): ǔ 2.3; IR v_{max} cm^{-1}: 3141, 2956, 2728, 1895,1595, 1492, 1393, 1224, 1026, 977, 831, 566; MS (ESI) m/z = 264 (M+H)$^+$; HRMS m/z (ESI) calculated for $C_{10}H_{16}O_3NClP$ (M+H)$^+$: 264.05508, found: 264.05381.

Methyl 3-(diethoxyphosphoryloxy)but-2-enoate (8h):
Yellow oil; 114 mg (45%); ^{1}H NMR δ (300 MHz, $CDCl_3$): 5.32 (s, 1H), 4.24-4.29 (m, 4H), 3.68 (s, 3H), 2.18 (s, 3H), 1.32 (t, *J* = 7.0 Hz, 6H) . ^{13}C NMR δ (125 MHz, $CDCl_3$): 164.0, 158.3 (d, *J* = 7.2 Hz), 104.9 (d, *J* = 8.1 Hz), 64.8 (d, *J* = 6.3 Hz), 51.0, 21.6, 16.0 (d, *J* = 7.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): ǔ -8.7; IR v_{max} cm^{-1}: 3477, 2988, 1728, 1670, 1441, 1277, 1216, 1157, 1018, 914; MS (ESI) m/z = 253 (M+H)$^+$; HRMS m/z (ESI) calculated for $C_9H_{18}O_6P$ (M+H)$^+$: 253.08355, found: 253.08223.

Ethyl 3-(diethoxyphosphoryloxy)but-2-enoate (8i):
Yellow oil; 85 mg (32%); ^{1}H NMR δ (300 MHz, $CDCl_3$): 5.31 (s, 1H), 4.22-4.31 (m, 4H), 4.15 (q, *J* = 7.5 Hz, 2H), 2.17 (d, *J* = 1.51 Hz, 3H), 1.37 (t, *J* = 6.7 Hz, 6H), 1.26 (t, *J* = 7.5 Hz, 3H) .^{13}C NMR δ (125 MHz, $CDCl_3$): 163.6,158.0 (d, *J* = 6.3 Hz), 105.4 (d, *J* = 9.0 Hz), 64.8 (d, *J* = 6.3 Hz), 59.7, 21.6, 16.0 (d, *J* = 6.3 Hz), 14.2. ^{31}P NMR (162 MHz, $CDCl_3$, ppm): ǔ -8.6; IR v_{max} cm^{-1}: 3456, 2985, 1725, 1667, 1444, 1277, 1213, 1153, 1026, 994; MS (ESI) m/z = 267 (M+H)$^+$; HRMS m/z (ESI) calculated for $C_{10}H_{20}O_6P$ (M+H)$^+$: 267.09920, found: 267.09784.

Tert-butyl 3-(diethoxyphosphoryloxy)but-2-enoate (8j):
Yellow oil; 83 mg (28%); ^{1}H NMR δ (300 MHz, $CDCl_3$): 5.25 (s, 1H), 4.20-4.30 (m, 4H), 2.13 (s, 3H), 1.46 (s, 9H), 1.37 (t, *J* = 6.7 Hz, 6H). **^{13}C** NMR δ (125 MHz, $CDCl_3$): 162.9, 156.6 (d, *J* = 6.6 Hz), 107.2 (d, *J* = 8.0 Hz), 80.0, 64.7 (d, *J* = 5.8 Hz), 28.1, 21.5, 16.6 (d, J=6.6 Hz), ^{31}P NMR (162 MHz, $CDCl_3$, ppm): ǔ -8.5; IR v_{max} cm^{-1}: 3470, 2982, 1719, 1666, 1445, 1281, 1228, 1150, 1029; MS (ESI) m/z = 295 (M+H)$^+$; HRMS m/z (ESI) calculated for $C_{12}H_{24}O_6P$ (M+H)$^+$: 295.13050, found: 295.12900.

Ethyl 3-(diethoxyphosphoryloxy)-3-phenylacrylate (8k):
Yellow oil; 76 mg (23%); ^{1}H NMR δ (300 MHz, $CDCl_3$): 7.6 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 5.6 Hz, 3H), 6.00 (d, *J* = 1.5 Hz, 1H), 4.10-4.27 (m, 6H), 1.32 (t, *J* = 6.9 Hz, 3H), 1.26 (t, *J* = 7.7 Hz, 6H).^{13}C NMR δ (125 MHz, $CDCl_3$): 164.0, 156.8 (d, *J* = 7.3 Hz), 133.9, 130.7, 128.4, 126.9, 106.5 (d, *J* = 6.6 Hz), 64.8 (d, *J* = 5.8 Hz), 60.2, 16.0 (d, *J* = 7.3 Hz), 14.2. ^{31}P NMR (162 MHz, $CDCl_3$, ppm): ǔ -7.8; IR v_{max} cm^{-1}: 3475, 2984, 1723, 1642, 1447, 1275, 1169, 1024, 977; MS (ESI) m/z = 329 (M+H)$^+$; HRMS m/z (ESI) calculated for $C_{15}H_{22}O_6P$ (M+H)$^+$: 329.11485, found: 329.11343.

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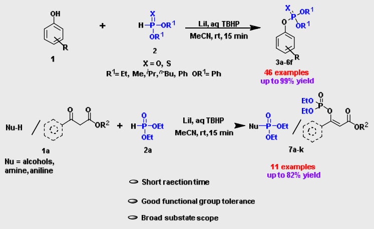

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