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Cetyltrimethyl ammonium bromide catalysed oxidative cross dehydrogenative coupling of benzylic C(sp^3)–H bonds in methylarenes with P(O)–OH compounds†

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An efficient metal-free method for the synthesis of organophosphorus compounds *via* oxidative cross dehydrogenative coupling of benzylic C(sp^3)–H bonds in methylarenes with P(O)–OH compounds catalysed by cetyltrimethyl ammonium bromide (CTAB) is reported. Various methylarenes and P(O)–OH compounds are tolerated in the reaction with moderate to good yields. Compared to previous studies, the present study extends the substrate scope and adopts a new reaction system of an ammonium salt catalyst (CTAB) and an oxidant (DTBP). The results of control and mechanistic experiments are generally in agreement with the overall proposed pathway. This method circumvents the use of toxic P–halogen reagents and P(O)–H compounds for the synthesis of organophosphorus compounds.

Introduction

Cetyltrimethyl ammonium bromide (CTAB) has been extensively investigated as a surface-active agent for a number of decades and is widely used as a wetting agent in food chemistry and as an emulsifier and plasticizer in industrial processes.[1a–c] Furthermore, this compound has received much attention in the field of heterogeneous catalysis and biology;[1d–f] it is used as a mesopore template in the preparation of catalysts[2a–b] as well as an agent to modify montmorillonite (MMT)[3] and bentonite (ACMB).[4] In contrast, the application of CTAB in homogeneous catalysis is undisclosed. Herein, we report an efficient metal-free method for the synthesis of organophosphorus compounds based on CTAB-catalysed oxidative cross dehydrogenative coupling of benzylic C(sp^3)–H bonds in methylarenes with P(O)–OH compounds.

The generation of organophosphorus compounds is of great importance in synthetic chemistry because these kinds of compounds are found in numerous biological, pharmaceutical, and material substances.[5–8] Traditionally, these compounds are prepared by nucleophilic substitution of toxic halides P(O)–X with alcohol or phenol derivatives.[9,10] With the major advances of Atherton–Todd reactions, it appears that there is a clean and straightforward approach to construct phosphate ester derivatives. For example, the direct catalytic P(O)–H/Nu–H cross dehydrogenative coupling (CDC) strategy that led to successful iodine-catalysed phosphorylation of alcohols reported by Dhineshkumar and Prabhu,[11] and the iron-catalysed dehydrogenative coupling of alcohols with P(O)–H compounds by Chen and Han.[12] As another appealing option for the synthesis of phosphate ester compounds, the direct P(O)–H/C–H cross dehydrogenative coupling should be an efficient approach. For instance, using unprocessed toluene derivatives as starting substrates and tetrabutylammonium iodide (Bu_4NI) as a catalyst, Tang and coworkers successfully synthesized phosphorus esters *via* phosphorylation of benzyl C–H bonds.[13] Despite the progress, the synthetic methods are somewhat restricted by the prerequisite of substrates that are air and moisture sensitive. Therefore, continuous efforts have been made to circumvent this hurdle. Most recently, through C(sp^3)–H bond phosphorylation of methyl-substituted arenes using Bu_4NI as a catalyst, Xiong *et al.* expanded the metal-free synthetic process to relatively inexpensive and stable substrates, namely, diarylphosphinic acids.[14] Nevertheless, this method is only compatible with aryl phosphinic acids and compounds that contain primary C(sp^3)–H, and the cross coupling of inert phosphoric diesters and non-primary

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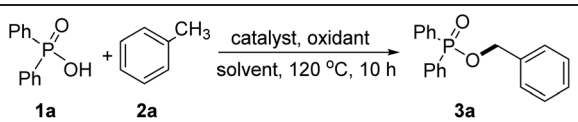
benzylic C(sp^3)–H based on this method was found unsatisfactory. Hence, the development of an efficient metal-free method that is diversely substrate-tolerant for the synthesis of organophosphorus compounds *via* oxidative C–H/P(O)OH cross dehydrogenative coupling is highly desired.

Results and discussion

Our initial investigation centred on the use of oxidizing reagents for the generation of suitable radical species. Diphenylphosphinic acid and toluene were employed as starting reagents. Also serving as a solvent, the latter was kept in excess. Various oxidizing reagents, such as TBHP, DCP, TBPB, BPO, DDQ, DTBP and H_2O_2, were tested (Table 1, entries 1–7).

Among them, DTBP was found to be the best, and to monitor its usage, its amount was varied from 4 equiv. to 0.5 equiv. (Table 1, entries 15–17). Furthermore, it was observed that the yield of **3a** is temperature dependent (Table 1, entries 7–11). To optimize the reaction conditions and to widen the application of the strategy, other catalysts and solvents were evaluated (Table 1, entries 19–24). The effects of catalyst loading were also studied (Table 1, entries 25–27). Ultimately, the optimal reaction conditions are as follows: diphenylphosphinic acid (0.1 mmol), toluene (0.5 ml), DTBP (4 equiv.) and CTAB (20 mol%) at 120 °C for 10 h under a nitrogen atmosphere.

Table 1 Optimization of reaction conditions



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

Entry	Catalyst	Oxidant	Solvent	Yield (%)
1	CTAB (20 mol%)	TBHP (4 eq.)	Toluene	0
2	CTAB (20 mol%)	DCP (4 eq.)	Toluene	42
3	CTAB (20 mol%)	TBPB (4 eq.)	Toluene	0
4	CTAB (20 mol%)	BPO (4 eq.)	Toluene	0
5	CTAB (20 mol%)	DDQ (4 eq.)	Toluene	0
6	CTAB (20 mol%)	H_2O_2 (4 eq.)	Toluene	0
7[a]	CTAB (20 mol%)	DTBP (4 eq.)	Toluene	83
8[b]	CTAB (20 mol%)	DTBP (4 eq.)	Toluene	62
9[c]	CTAB (20 mol%)	DTBP (4 eq.)	Toluene	61
10[d]	CTAB (20 mol%)	DTBP (4 eq.)	Toluene	0
11[e]	CTAB (20 mol%)	DTBP (4 eq.)	Toluene	85
12[f]	CTAB (20 mol%)	DTBP (4 eq.)	Toluene	0
13	CTAB (20 mol%)	DTBP (4 eq.)	Toluene	88
14	CTAB (20 mol%)	—	Toluene	0
15	CTAB (20 mol%)	DTBP (2 eq.)	Toluene	0
16	CTAB (20 mol%)	DTBP (1 eq.)	Toluene	0
17	CTAB (20 mol%)	DTBP (50 mol%)	Toluene	0
18	—	DTBP (4 eq.)	Toluene	0
19	CTAB (20 mol%)	DTBP (4 eq.)	EtOH	0
20	CTAB (20 mol%)	DTBP (4 eq.)	H_2O	0
21	CTAB (20 mol%)	DTBP (4 eq.)	IPA	0
22	TBAI (20 mol%)	DTBP (4 eq.)	Toluene	0
23	TBAB (20 mol%)	DTBP (4 eq.)	Toluene	4
24	TBAC (20 mol%)	DTBP (4 eq.)	Toluene	0
25	CTAB (10 mol%)	DTBP (4 eq.)	Toluene	Trace
26	CTAB (5 mol%)	DTBP (4 eq.)	Toluene	0
27	CTAB (1 mol%)	DTBP (4 eq.)	Toluene	0

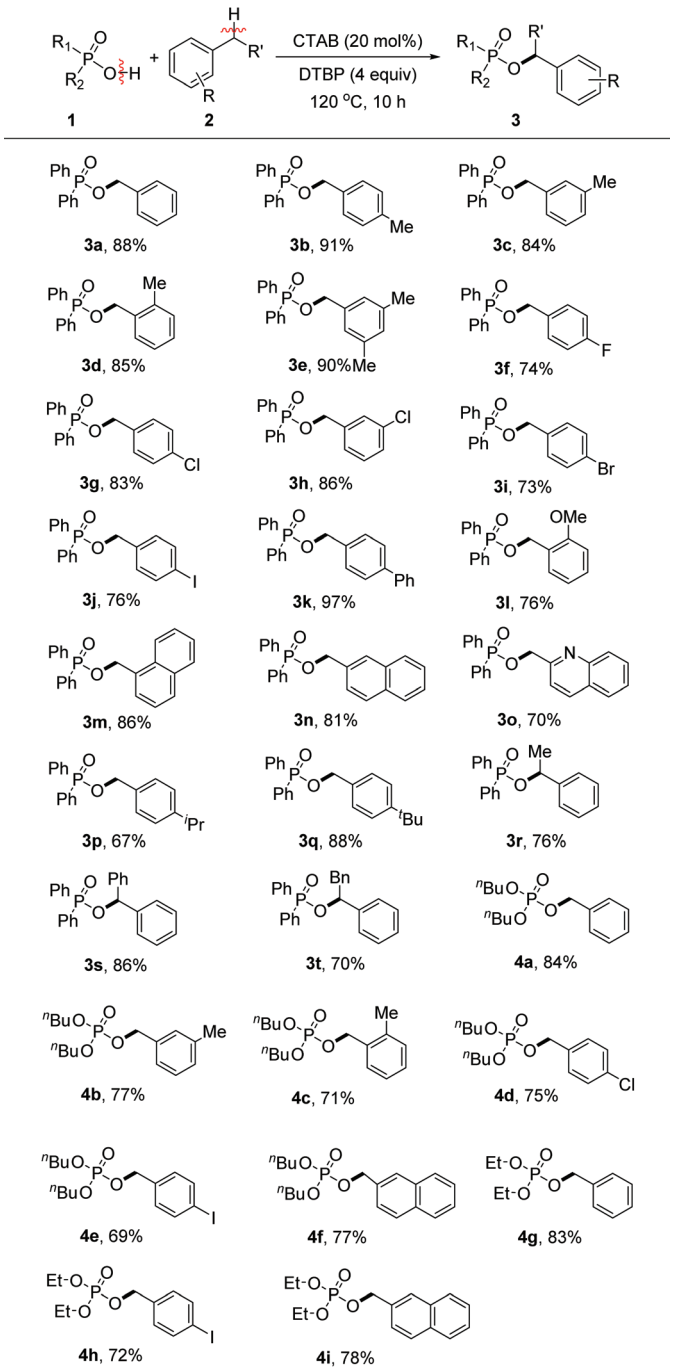
Reaction conditions: Diphenylphosphinic acid (0.1 mmol), toluene (0.5 ml), 120 °C, 10 h. Yield was determined by ^{31}P NMR spectroscopy; CTAB (20 mol%); TBHP = *tert*-butylhydroperoxide 70% in water; H_2O_2 30% in water; DTBP = di-*t*-butylperoxide. [a] 140 °C. [b] 100 °C. [c] 80 °C. [d] 60 °C. [e] 16 h. [f] In air.

With the optimized conditions in hand, we turned to explore other kinds of substrates (Table 2). A variety of functional groups such as methyl (**3b–3e**), fluoro (**3f**), chloro (**3g** and **3h**), bromo (**3i**), iodo (**3j**), phenyl (**3k**), and methoxyl (**3l**) are well-tolerated under the standard conditions. It is noted that steric methylnaphthalenes (**3m** and **3n**) and inert 2-methylquinoline (**3o**) are compatible, giving the corresponding products in moderate to good yields. In the cases of mesitylene (**3e**), *p*-cymene (**3p**) and 1-(*tert*-butyl)-4-methylbenzene (**3q**), the reaction exclusively occurs at the primary benzylic C(sp^3)–H bond. In addition, the substrates without a primary benzylic C(sp^3)–H bond, such as ethylbenzene (**3r**), diphenylmethane (**3s**) and 1,2-diphenylethane (**3t**), are found suitable for this reaction. Overall, the results indicate that the protocol has circumvented the limitations of the previously reported methods.[13] Moreover, the reaction works well for an array of phosphoric diesters. For instance, diethyl hydrogen phosphate and dibutyl hydrogen phosphate react smoothly with numerous toluene derivatives bearing either electron-donating or electron-withdrawing groups as in the cases of methylnaphthalenes (**4f** and **4i**). The presence of steric hindrance has little effect on the efficiency of the reaction, as illustrated in the cases of **4f** and **4i**.

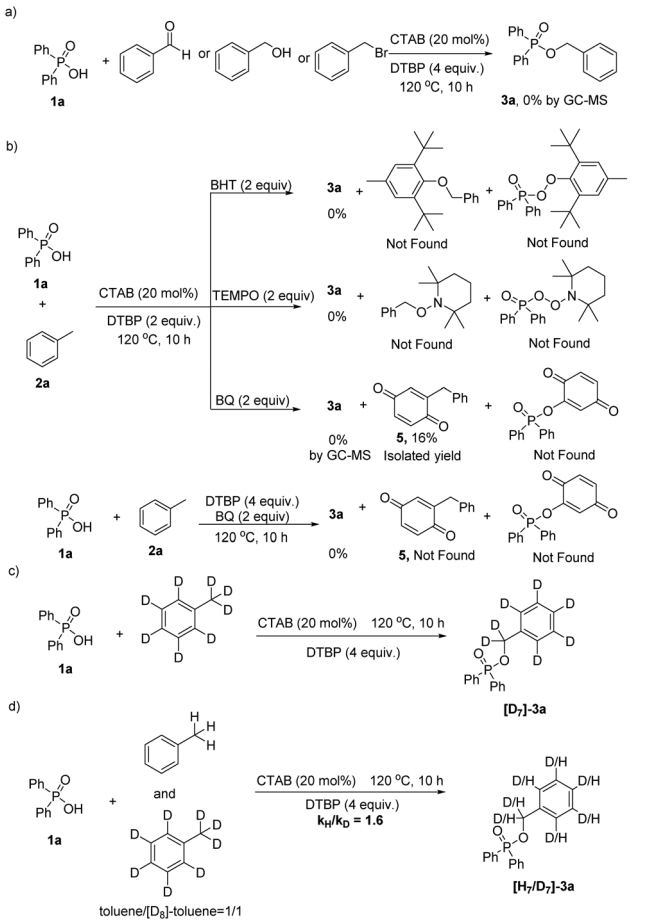
In order to gain insight into the reaction mechanism, control experiments were performed (see the ESI† for details). To begin with, benzyl alcohol, benzyl aldehyde or benzyl bromide was assumed to be a potential intermediate in the reaction. Nonetheless, replacing toluene with benzyl alcohol, benzyl aldehyde or benzyl bromide did not yield the desired product (Scheme 1a), contradicting the possibility that benzyl alcohol, benzyl aldehyde or benzyl bromide is an intermediate in this reaction. When a radical scavenger, such as 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO), 2,6-di-*tert*-butyl-4-methylphenol (BHT) or 1,4-benzoquinone (BQ), was added into the reaction of **1a** with toluene under the optimal conditions, there was no generation of the desired product (Scheme 1b). The phenomenon confirms the involvement of radicals in this reaction. Finally, an intermolecular competition experiment between toluene and toluene-d_8 was performed, with k_H/k_D values up to 1.6 (Scheme 1c), indicating that hydrogen abstraction of toluene is rate-determining in this reaction.

According to the above results, we deduce that the reaction is initiated by CTAB and DTBP through the formation of benzyl radicals. Furthermore, on the basis of the results reported by Shi and coworkers,[15a,b] we speculate that during the reaction the benzyl radicals are oxidized to benzyl cations. Based on the above criteria, a plausible catalytic cycle is proposed as presented in Scheme 2. Initially, the reaction between CTAB and DTBP gives the active intermediate ammonium **6** ($[(C_{19}H_{42})N]^+[BrO]^-$) or **7** ($[(C_{19}H_{42})N]^+[BrO_2]^-$) that is able to

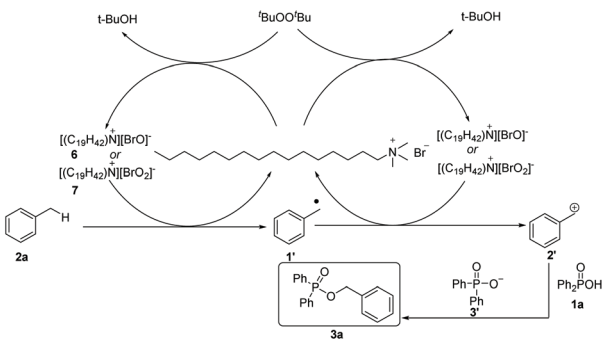
Table 2 CTAB-catalysed oxidative cross dehydrogenative coupling of methylarenes with P(O)–OH compounds



Reaction conditions: Diphenylphosphinic acid (0.1 mmol), toluene (0.5 ml), DTBP (0.4 mmol), CTAB (20 mol%), 120 °C, 10 h. Yield was determined by ^{31}P NMR spectroscopy.



Scheme 1 Control experiments.



Scheme 2 Proposed reaction mechanism.

activate the benzyl C–H bond for the generation of a benzylic radical. This is the rate-determining step in the whole reaction. The single electron of hydrogen could be captured by either **6** or **7** to regenerate CTAB. Nevertheless, the benzyl radical could be simultaneously oxidized by **6** or **7** to form a benzylic cation that would couple with diphenylphosphinic acid to give the corresponding product **3a**.

Conclusions

In this paper, we developed a practical metal-free method for the synthesis of organophosphorus compounds based on CTAB-catalysed oxidative cross dehydrogenative coupling of

benzylic C(sp^3)–H bonds in methylarenes with P(O)–OH compounds. The protocol is simple and can circumvent the limitations of the previously reported methods. It tolerates a wide range of functional groups, delivering organophosphorus compounds in moderate to excellent yields. Moreover, different types of C(sp^3)–H bonds, no matter primary or secondary, can couple with phosphinic acids or phosphoric diesters. The results of control and mechanistic experiments are generally in agreement with the proposed pathway. This versatile protocol should provide a new avenue for the synthesis of phosphate esters with wide applications in the fields of biological, pharmaceutical, and materials chemistry.

Experimental

General experimental procedures

The reactions were carried out in 25 mL Schlenk tubes under N_2. Unless otherwise noted, the materials from commercial suppliers were used without further purification, whereas the solvents were purified according to standard operating procedures. Flash column chromatography was performed using Silica Gel 60 (300–400 mesh). Analytical thin layer chromatography (TLC) was performed on Haiyang TLC silica gel GF254 (0.25 mm) plates. The ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a Bruker ADVANCE III spectrometer operating at 400 MHz, 100 MHz and 162 MHz respectively; and chemical shifts were reported in ppm (δ) relative to internal tetramethylsilane (TMS). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (J) were reported in hertz. The NMR yields were determined by ^{31}P NMR with triphenylphosphine oxide (at 29.0 ppm) as the internal standard. The reactions were monitored using GC-MS QP 2010 equipment. The electron ionization (EI) approach was used as the ionization method for HRMS measurement. Fourier transform infrared spectroscopy (FT-IR, Thermo Nicolet) was used to explore the chemical bonds of the products.

General procedure for the synthesis of organophosphorus compounds

To a 25 mL Schlenk tube, a mixture of P(O)–OH compound (0.1 mmol), CTAB (20 mol%), DTBP (0.4 mmol) and methylarenes (0.5 ml) was added with magnetic stirring at room temperature. With constant stirring the mixture was heated to 120 °C and kept at this temperature for 10 h. Then the reaction solution was allowed to cool to ambient temperature, and then transferred to a round-bottom flask. Silica gel (4.0 g) was added, and the solvent was removed under reduced pressure to afford a free-flowing powder. This powder was then dry-loaded onto a silica gel column and purified by flash chromatography using petroleum ether/ethyl acetate (5/1–2/1, v/v) as the eluent to give the corresponding products.

Benzyl diphenylphosphinate (3a). Colorless oil,[13,14] R_f = 0.20 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.84 (m, 4H), 7.54–7.31 (m, 11H), 5.09 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2 (d, J = 7.4 Hz), 132.1 (d, J = 2.7 Hz), 131.5 (d, J = 10.0 Hz), 131.2 (d, J = 135.9 Hz), 128.4 (d, J = 8.2 Hz), 128.3 (s), 128.1 (s), 127.7 (s), 66.1 (d, J = 5.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.17 (d, J = 19.1 Hz). MS-ESI: m/z 331.12, $[M + Na]^+$.

4-Methyl-benzyl diphenylphosphinate (3b). Colorless oil,[13,14] R_f = 0.35 (petroleum ether/ethyl acetate = 2 : 1), melting point: 87–88 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.71 (m, 4H), 7.41–7.32 (m, 6H), 7.16–7.03 (m, 4H), 4.93 (d, J = 6.76 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0 (s), 133.2 (d, J = 7.5 Hz), 132.0 (d, J = 2.8 Hz), 131.6 (d, J = 10.1 Hz), 131.3 (d, J = 135.7 Hz), 129.1 (s), 128.5 (s), 128.3 (s), 127.9 (s), 66.2 (d, J = 5.6 Hz), 21.1 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1 (s). MS-ESI: m/z 345.14, $[M + Na]^+$.

3-Methyl-benzyl diphenylphosphinate (3c). Yellow oil,[14] R_f = 0.45 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.81 (m, 4H), 7.53–7.44 (m, 6H), 7.25–7.11 (m, 4H), 5.03 (d, J = 4.8 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1 (s), 136.1 (d, J = 7.4 Hz), 132.1 (d, J = 2.9 Hz), 131.7 (d, J = 10.1 Hz), 131.3 (d, J = 135.9 Hz), 129.0 (s), 128.7 (s), 128.6 (s), 128.5 (d, J = 13.0 Hz), 125.0 (s), 66.3 (d, J = 5.4 Hz), 21.3 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3 (s).

2-Methyl-benzyl diphenylphosphinate (3d). Colorless oil,[13] R_f = 0.52 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.70 (m, 4H), 7.42–7.39 (m, 2H), 7.35–7.30 (m, 4H), 7.22 (d, J = 7.4 Hz, 1H), 7.13–7.05 (m, 3H), 4.99 (d, J = 6.2 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6 (s), 134.2 (d, J = 7.6 Hz), 132.1 (d, J = 2.9 Hz), 131.5 (d, J = 10.2 Hz), 131.7 (d, J = 135.6 Hz), 130.2 (s), 128.5 (d, J = 15.0 Hz), 128.5 (s), 128.4 (s), 125.9 (s), 64.6 (d, J = 5.5 Hz), 18.9 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3 (s). HRMS-ESI: m/z 345.1023, ($[M + Na]^+$, $C_{20}H_{19}NaO_2P^+$ calcd 345.1030).

3,5-Dimethylbenzyl diphenylphosphinate (3e). Yellow oil,[13] R_f = 0.55 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.69 (m, 4H), 7.35–7.28 (m, 6H), 6.83–6.80 (m, 3H), 4.87 (d, J = 7.0 Hz, 2H), 2.14 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8 (s), 135.8 (d, J = 7.3 Hz), 131.9 (d, J = 2.9 Hz), 131.4 (d, J = 10.1 Hz), 131.2 (d, J = 136.1 Hz), 130.0 (s), 128.2 (d, J = 13.1 Hz), 125.6 (s), 66.2 (d, J = 5.5 Hz), 21.0 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1 (s). HRMS-ESI: m/z 359.1180. ($[M + Na]^+$, $C_{21}H_{21}NaO_2P^+$ calcd 359.1166).

4-Fluoro-benzyl diphenylphosphinate (3f). Yellow oil,[13,14] R_f = 0.45 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.67 (m, 4H), 7.36–7.17 (m, 8H), 6.88–6.84 (m, 2H), 4.90 (d, J = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, J = 245.4 Hz), 132.0 (d, J = 2.8 Hz), 131.9 (d, J = 3.3 Hz), 131.3 (d, J = 10.1 Hz), 131.0 (d, J = 135.7 Hz), 129.6 (d, J = 8.1 Hz), 128.3 (d, J = 13.1 Hz), 115.1 (d, J = 21.4 Hz), 65.3 (d, J = 5.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4 (s). HRMS-ESI: m/z 349.0774, ($[M + Na]^+$, $C_{19}H_{16}FNaO_2P^+$ calcd 349.0780).

4-Chlorobenzyl diphenylphosphinate (3g). Yellow oil,[13,14] R_f = 0.55 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.67 (m, 4H), 7.35–7.29 (m, 6H),

7.14 (s, 4H), 4.88 (d, J = 5.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6 (d, J = 7.2 Hz), 133.8 (s), 132.0 (d, J = 2.8 Hz), 131.3 (d, J = 10.2 Hz), 130.8 (d, J = 135.7 Hz), 128.9 (s), 128.4 (s), 128.2 (s), 65.2 (d, J = 5.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6 (s). HRMS-ESI: m/z 365.0473, ([M + Na]$^+$, $C_{19}H_{16}ClNaO_2P^+$ calcd 365.0464).

3-Chlorobenzyl diphenylphosphinate (3h). Yellow oil,[14] R_f = 0.48 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 4H), 7.55–7.46 (m, 6H), 7.34 (s, 1H), 7.28–7.24 (m, 3H), 5.03 (d, J = 7.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4 (d, J = 7.3 Hz), 134.4 (s), 132.3 (d, J = 2.8 Hz), 131.6 (d, J = 10.2 Hz), 130.3 (s), 130.0 (s), 129.1 (d, J = 144.8 Hz), 128.6 (d, J = 13.1 Hz), 127.8 (s), 125.8 (s), 65.3 (d, J = 5.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8 (s). HRMS-ESI: m/z calcd for $C_{19}H_{16}ClO_2P$: 342.0576 found 342.0575.

4-Bromobenzyl diphenylphosphinate (3i). Yellow oil,[13,14] R_f = 0.47 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 4H), 7.51–7.44 (m, 8H), 7.23 (d, J = 8.8 Hz, 2H), 5.00 (d, J = 8.76 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2 (d, J = 7.1 Hz), 132.2 (d, J = 2.9 Hz), 131.5 (d, J = 1.7 Hz), 131.4 (s), 131.0 (d, J = 135.8 Hz), 129.4 (s), 128.4 (d, J = 13.1 Hz), 122.1 (s), 65.4, (d, J = 5.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7 (s). MS-ESI: m/z 409.14, [M + Na]$^+$.

4-Iodobenzyl diphenylphosphinate (3j). Yellow oil,[13,14] R_f = 0.45 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.69 (m, 4H), 7.55–7.50 (m, 2H), 7.39–7.31 (m, 6H), 7.00–6.96 (m, 2H), 4.89 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4 (s), 135.8 (d, J = 6.9 Hz), 132.2 (d, J = 2.9 Hz), 131.4 (d, J = 10.3 Hz), 130.9 (d, J = 135.8 Hz), 129.5 (s), 128.4 (d, J = 13.2 Hz), 93.9 (s), 65.4 (d, J = 5.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7 (d, J = 8.6 Hz). HRMS-ESI: m/z 456.9833, ([M + Na]$^+$, $C_{19}H_{16}INaO_2P^+$ calcd 456.9831).

[1,1′-Biphenyl]-4-ylmethyl diphenylphosphinate (3k). Yellow oil,[13] R_f = 0.35 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.70 (m, 4H), 7.43–7.41 (m, 4H), 7.34–7.25 (m, 10H), 7.19–7.15 (m, 1H), 4.97 (d, J = 6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0 (s), 140.3 (s), 135.1 (d, J = 7.2 Hz), 132.0 (d, J = 2.7 Hz), 131.4 (d, J = 10.1 Hz), 131.1 (d, J = 135.8 Hz), 128.6 (s), 128.4 (s), 128.2 (d, J = 9.7 Hz), 127.2 (s), 127.0 (s), 126.8 (s), 65.9 (d, J = 5.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4 (s). MS-ESI: m/z 407.14, [M + Na]$^+$.

2-Methoxybenzyl diphenylphosphinate (3l). Yellow oil, R_f = 0.43 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.73 (m, 4H), 7.42–7.33 (m, 7H), 7.21–7.17 (m, 1H), 6.87–6.84 (m, 1H), 6.73 (d, J = 8.2 Hz, 1H), 5.05 (d, J = 6.3 Hz, 2H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0 (s), 132.0 (d, J = 2.9 Hz), 131.5 (d, J = 136.2 Hz), 131.6 (d, J = 10.2 Hz), 129.4 (s), 129.0 (s), 128.4 (s), 128.3 (s), 124.7 (d, J = 7.9 Hz), 120.3 (s), 110.1 (s), 61.8 (d, J = 5.2 Hz), 55.1 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1 (s). HRMS-ESI: m/z 361.0992, ([M + Na]$^+$, $C_{20}H_{19}NaO_3P^+$ calcd 361.0990). IR (neat): ν = 2928, 2824, 1593, 1248, 1290, 1257, 1034 cm^{-1}.

(Naphthalen-1-yl)methyl diphenylphosphinate (3m). Yellow oil,[14] R_f = 0.39 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.1 Hz, 1H), 7.71–7.66 (m, 6H), 7.41–7.31 (m, 5H), 7.27–7.23 (m, 5H), 5.41 (d, J = 6.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.5 (s), 132.1 (d, J = 2.7 Hz), 131.7 (d, J = 7.4 Hz), 131.7 (d, J = 10.2 Hz), 131.1 (d, J = 135.5 Hz), 129.2 (s), 128.5 (s), 128.4 (s), 128.3 (s), 126.7 (s), 126.4 (s), 125.8 (s), 125.0 (s), 123.4 (s), 64.6 (d, J = 5.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5 (s).

(Naphthalen-2-yl)methyl diphenylphosphinate (3n). Yellow oil,[13,14] R_f = 0.45 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.67 (m, 8H), 7.41–7.37 (m, 9H), 5.13 (d, J = 6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7 (d, J = 7.4 Hz), 133.1 (d, J = 2.3 Hz), 132.2 (d, J = 2.8 Hz), 131.7 (s), 131.6 (s), 131.3 (d, J = 135.7 Hz), 128.6 (s), 128.4 (s), 128.0 (s), 127.6 (s), 127.0 (s), 126.2 (s), 126.2 (s), 125.6 (s), 66.5 (d, J = 5.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5 (s). HRMS-ESI: m/z 381.1024, ([M + Na]$^+$, $C_{23}H_{19}NaO_2P^+$ calcd 381.1021).

Quinolin-2-ylmethyl diphenylphosphinate (3o). Yellow oil,[13] R_f = 0.22 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.5 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.85–7.75 (m, 4H), 7.76 (d, J = 8.3 Hz, 1H), 7.68–7.63 (m, 2H), 7.50–7.45 (m, 3H), 7.41–7.37 (m, 4H), 5.27 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6 (d, J = 8.0 Hz), 147.1 (s), 137.3 (s), 132.4 (d, J = 2.9 Hz), 131.7 (d, J = 10.2 Hz), 130.9 (d, J = 136.3 Hz), 129.4 (d, J = 114.4 Hz), 128.7 (s), 128.6 (s), 127.6 (s), 127.6 (s), 126.8 (s), 119.5 (s), 67.3 (d, J = 5.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.4 (s). HRMS-ESI: m/z 382.0976, ([M + Na]$^+$, $C_{22}H_{18}NNaO_2P^+$ calcd 382.0972).

4-Isopropylbenzyl diphenylphosphinate (3p). Yellow oil, R_f = 0.55 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.72 (m, 4H), 7.44–7.40 (m, 2H), 7.36–7.35 (m, 4H), 7.22–7.11 (m, 4H), 4.95 (d, J = 5.8 Hz, 2H), 2.87–2.76 (m, 1H), 1.15 (d, J = 5.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1 (s), 133.7 (d, J = 7.7 Hz), 132.1 (d, J = 2.9 Hz), 131.4 (d, J = 135.8 Hz), 131.7 (d, J = 10.1 Hz), 128.5 (d, J = 13.1 Hz), 128.1 (s), 126.6 (s), 66.3 (d, J = 5.6 Hz), 33.9 (s), 23.9 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3 (s). HRMS-ESI: m/z 373.1412, ([M + Na]$^+$, $C_{22}H_{23}NaO_2P^+$ calcd 373.1402). IR (neat): ν = 2917, 1601, 1374, 1280, 1223, 1011 cm^{-1}.

4-(*tert*-Butyl)benzyl diphenylphosphinate (3q). Yellow oil,[14] R_f = 0.60 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76–7.72 (m, 4H), 7.42–7.38 (m, 2H), 7.34–7.31 (m, 4H), 7.28–7.20 (m, 4H), 4.95 (d, J = 6.7 Hz, 2H), 1.21 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2 (s), 133.2 (d, J = 7.5 Hz), 132.1 (d, J = 2.9 Hz), 131.6 (d, J = 10.2 Hz), 131.3 (d, J = 135.8 Hz), 128.4 (d, J = 13.1 Hz), 127.7 (s), 125.4 (s), 66.1 (d, J = 5.5 Hz), 34.5 (s), 31.2 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1 (s).

1-Phenylethyl diphenylphosphinate (3r). Yellow oil,[13] R_f = 0.63 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.83 (m, 2H), 7.69–7.64 (m, 2H), 7.49–7.40 (m, 4H), 7.30 (s, 7H), 5.56–5.49 (m, 1H), 1.66 (d, J = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9 (d, J = 5.1 Hz), 132.5 (d, J = 93.5 Hz), 131.9 (d, J = 2.8 Hz), 131.8 (d, J = 2.8 Hz), 131.7 (d, J = 10.2 Hz), 131.3 (d, J = 10.0 Hz), 131.1 (d, J = 88.4 Hz), 128.4 (s), 128.3 (s), 128.2 (s), 128.2 (s), 128.1 (s), 74.4 (d, J = 5.6 Hz), 24.9 (d, J = 3.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.1 (s). HRMS-ESI: m/z 345.1021, ([M + Na]$^+$, $C_{20}H_{19}NaO_2P^+$ calcd 345.1021).

Benzhydryl diphenylphosphinate (3s). Yellow oil,[16] R_f = 0.65 (petroleum ether/ethyl acetate = 2 : 1), melting point: 302–303 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.61 (m, 4H), 7.37–7.34 (m, 2H), 7.25–7.14 (m, 14H), 6.40 (d, J = 10.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6 (d, J = 4.1 Hz), 131.9 (d, J = 2.5 Hz), 131.7 (d, J = 10.2 Hz), 131.5 (d, J = 136.2 Hz), 128.3 (s), 128.1 (s), 127.8 (s), 127.1 (s), 78.5 (d, J = 5.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3 (s). HRMS-ESI: m/z 407.1194, ($[M + Na]^+$, $C_{25}H_{21}NaO_2P^+$ calcd 407.1190).

1,2-Diphenylethyl diphenylphosphinate (3t). Yellow oil,[17] R_f = 0.60 (petroleum ether/ethyl acetate = 2 : 1), melting point: 141–142 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.61 (m, 4H), 7.53–7.49 (m, 1H), 7.42–7.38 (m, 3H), 7.32–7.28 (m, 2H), 7.24–7.19 (m, 8H), 7.03 (s, 2H), 5.55 (q, J = 7.5 Hz, 1H), 3.42 (dd, J = 13.6, 6.4 Hz, 1H), 3.24 (dd, J = 13.6, 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9 (d, J = 3.6 Hz), 136.4 (s), 132.3 (d, J = 47.0 Hz), 131.9 (d, J = 2.9 Hz), 131.8 (s), 131.8 (d, J = 0.2 Hz), 131.7 (s), 131.4 (d, J = 10.2 Hz), 131.0 (d, J = 43.7 Hz), 129.9 (s), 128.4 (s), 128.2 (d, J = 6.3 Hz), 128.0 (s), 127.9 (s), 126.6 (s), 126.5 (s), 78.9 (d, J = 5.9 Hz), 45.2 (d, J = 4.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.5 (s). HRMS-ESI: m/z 421.1289, ($[M + Na]^+$, $C_{26}H_{23}NaO_2P^+$ calcd 421.1287).

Benzyl dibutyl phosphate (4a). Yellow,[13] R_f = 0.75 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 5H), 4.98 (d, J = 8.4 Hz, 2H), 3.93 (d, J = 7.2 Hz, 4H), 1.58–1.52 (m, 4H), 1.34–1.27 (m, 4H), 0.85–0.81 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.0 (d, J = 6.7 Hz), 128.3 (s), 128.2 (s), 127.6 (s), 68.8 (d, J = 5.4 Hz), 67.3 (d, J = 6.2 Hz), 32.0 (d, J = 6.9 Hz), 18.4 (s), 13.4 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.7 (s). MS-ESI: m/z 323.12, $[M + Na]^+$.

Dibutyl(3-methylbenzyl)phosphate (4b). Yellow oil,[18] R_f = 0.77 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.15 (m, 4H), 5.03 (d, J = 8.3 Hz, 2H), 4.05–4.00 (m, 4H), 2.35 (s, 3H), 1.65–1.61 (m, 4H), 1.43–1.35 (m, 4H), 0.94–0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1 (s), 135.9 (d, J = 6.6 Hz), 129.0 (s), 128.4 (s), 128.3 (s), 124.8 (s), 68.9 (d, J = 5.6 Hz), 67.3 (d, J = 5.9 Hz), 32.1 (d, J = 6.9 Hz), 21.2 (s), 18.5 (s), 13.4 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.7 (s).

Dibutyl(2-methylbenzyl)phosphate (4c). Yellow oil,[18] R_f = 0.49 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.17 (m, 4H), 5.08 (d, J = 7.6 Hz, 2H), 4.04–3.99 (m, 4H), 2.37–2.33 (m, 3H), 1.64–1.58 (m, 4H), 1.42–1.35 (m, 4H), 0.93–0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5 (s), 133.9 (d, J = 7.0 Hz), 130.1 (s), 128.6 (s), 128.5 (s), 125.8 (s), 67.2 (d, J = 6.1 Hz), 67.1 (d, J = 6.0 Hz), 32.0 (d, J = 6.7 Hz), 18.5 (d, J = 3.1 Hz), 18.4 (s), 13.3 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.69 (s).

Dibutyl(4-chlorobenzyl)phosphate (4d). Yellow oil, R_f = 0.40 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 4H), 5.03 (d, J = 8.6 Hz, 2H), 4.04–3.99 (m, 4H), 1.66–1.59 (m, 4H), 1.42–1.33 (m, 4H), 0.93–0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6 (d, J = 6.6 Hz), 134.3 (s), 129.1 (s), 128.7 (s), 68.1 (d, J = 5.4 Hz), 67.6 (d, J = 6.1 Hz), 32.2 (d, J = 6.9 Hz), 18.6 (s), 13.5 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.7 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3 (s). HRMS-ESI: m/z 357.0997, ($[M + Na]^+$, $C_{15}H_{24}ClNaO_4P^+$ calcd 357.0990). IR (neat): ν = 2928, 1609, 1269, 1053, 796 cm^{-1}.

Dibutyl(4-iodobenzyl)phosphate (4e). Yellow oil, R_f = 0.35 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 7.9 Hz, 2H), 4.92 (d, J = 8.5 Hz, 2H), 3.97–3.91 (m, 4H), 1.59–1.53 (m, 4H), 1.35–1.27 (m, 4H), 0.86–0.82 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5 (s), 135.7 (d, J = 6.6 Hz), 129.5 (s), 94.0 (s), 68.1 (d, J = 5.4 Hz), 67.5 (d, J = 6.0 Hz), 32.1 (d, J = 7.0 Hz), 18.5 (s), 13.5 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.74 (s). HRMS-ESI: m/z 449.0382, ($[M + Na]^+$, $C_{15}H_{24}INaO_4P^+$ calcd 449.0380). IR (neat): ν = 2928, 1560, 1271, 1034, 539 cm^{-1}.

Dibutyl(naphthalen-2-ylmethyl)phosphate (4f). Yellow oil,[19] R_f = 0.35 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.73 (m, 4H), 7.43–7.38 (m, 3H), 5.14 (d, J = 8.3 Hz, 2H), 3.96–3.91 (m, 4H), 1.56–1.49 (m, 4H), 1.32–1.22 (m, 4H), 0.81–0.77 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.4 (d, J = 6.6 Hz), 133.1 (s), 133.0 (s), 128.3 (s), 127.9 (s), 127.6 (s), 126.8 (s), 126.3 (s), 126.2 (s), 125.3 (s), 69.1 (d, J = 5.5 Hz), 67.5 (d, J = 6.1 Hz), 32.1 (d, J = 6.9 Hz), 18.5 (s), 13.4 (s). ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.60 (s).

Benzyl diethyl phosphate (4g). Yellow oil,[13] R_f = 0.50 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.35 (m, 5H), 5.07 (d, J = 8.2 Hz, 2H), 4.10–4.05 (m, 4H), 1.32–1.29 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1 (s), 128.5 (s), 128.4 (s), 127.8 (s), 69.0 (d, J = 5.5 Hz), 63.8 (d, J = 5.9 Hz), 16.0 (d, J = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.92 (s).

Diethyl(4-iodobenzyl)phosphate (4h). Yellow oil, R_f = 0.29 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.30–7.13 (m, 2H), 5.00 (d, J = 10.0 Hz, 2H), 4.13–4.06 (m, 4H), 1.33–1.29 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7 (s), 135.7 (d, J = 6.9 Hz), 129.6 (s), 94.1 (s), 68.2 (d, J = 5.4 Hz), 63.9 (d, J = 5.8 Hz), 16.1 (d, J = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.93 (s). HRMS-ESI: m/z 392.9821, ($[M + Na]^+$, $C_{11}H_{16}INaO_4P^+$ calcd 392.9814).

Diethyl(naphthalen-2-ylmethyl)phosphate (4i). Yellow oil,[13] R_f = 0.50 (petroleum ether/ethyl acetate = 2 : 1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 3.2 Hz, 4H), 7.49 (s, 3H), 5.23 (d, J = 8.2 Hz, 2H), 4.12–4.08 (m, 4H), 1.32–1.28 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.4 (d, J = 6.8 Hz), 133.1 (d, J = 8.3 Hz), 128.4 (s), 128.0 (s), 127.6 (s), 126.9 (s), 126.3 (s), 126.3 (s), 125.4 (s), 69.1 (d, J = 5.4 Hz), 63.8 (d, J = 5.8 Hz), 16.0 (d, J = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ −0.84 (s).

Conflicts of interest

There are no conflicts to declare.

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