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A palladium-catalyzed oxidative cross-coupling reaction between aryl pinacol boronates and *H*-phosphonates in ethanol†

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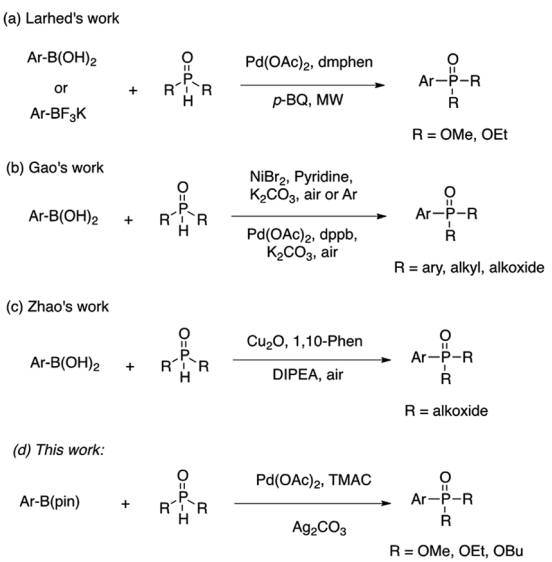
The first successful oxidative coupling reaction of aryl pinacol boronic esters with *H*-phosphonates to deliver aryl phosphorous compounds is reported herein. These reactions between aryl boronic reagents and *H*-phosphonates were carried out synergistically using a Pd catalyst, additive and oxidant. Without using bases and ligands, phosphorylation was accomplished in an environmentally-friendly manner under mild conditions in ethanol.

Introduction

The development of versatile methods for the synthesis of arylphosphorous compounds[1] has attracted much attention, owing to their broad applications in medicinal chemistry,[2] materials chemistry,[3] organic synthesis[4] and catalysis.[5] In 1981, Hirao and co-workers reported the first construction of C(sp^2)–P bonds through palladium-catalyzed cross-coupling of aryl halides with *H*-phosphonates.[6] During the past three decades, the scope of the reactions catalyzed by Pd, Cu and Ni or other metals reagents to form C(sp^2)–P bonds employing functionalized arenes with phosphorus reagents has been significantly expanded to various aryl halides,[7] triflates,[8] imidazolylsulfonates,[9] diazonium salts,[10] *o*-aryl silyl triflates,[11] arylhydrazines,[12] arylnitriles,[13] aryl pivalates,[14] sodium arylsulfinates[15] and diaryliodonium salts.[16] Arylphosphorus compounds can also be produced by the palladium or copper-catalyzed directed C–H/P(O)–H coupling reactions.[17]

Aryl boronic acids[18] are extensively used as substrates in transition-metal catalyzed cross-coupling reactions including Suzuki–Miyaura cross-coupling reactions,[19] Cu-catalyzed C–O, C–N, C–S and C–Se coupling reactions,[20] and Rh-catalyzed conjugate additions to carbonyl compounds,[21] owing to their commercial availability and structural diversity. There are only a few examples reported for C–P bond forming reactions using aryl boronic acids (Scheme 1a–c).[22] Notably, additional ligands and bases are required in these works. Aryl boronic esters, especially aryl pinacol boronates, have received a great deal of attention in the catalysis community. In general, aryl boronic esters exhibit greater chemical stability and readily soluble in aprotic solvents. In most cases, they also exhibit stability towards column chromatography, which aids in their ease of isolation and purification. In addition, many are liquids at room temperature and can be easily distilled. However, to the best of our knowledge, the preparation of arylphosphorus compounds *via* oxidative cross coupling reactions of aryl boronic esters with *H*-phosphonates has never been developed. Herein, we report the first coupling reaction of aryl pinacol boronic esters with *H*-phosphonates through palladium catalysis (Scheme 1d). The features of this system include that the reactions are performed in ethanol and also declined the requirement of external ligand and base. The most important feature that we observed was that the reaction conditions used



Scheme 1 Synthesis of aryl phosphorous compounds from arylboronic reagents.

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in Scheme 1a–c were not successful for the coupling of aryl pinacol boronate with *H*-phosphonate.

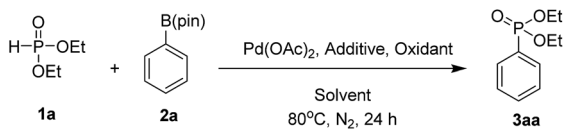
Results and discussion

We selected diethyl phosphite (**1a**) and phenyl pinacol boronate (**2a**) as model substrates to optimize the reaction conditions (Table 1). Initially, the reaction was carried out with $Pd(OAc)_2$ (5 mol%) as the catalyst and Ag_2CO_3 (1.5 equiv.) as the oxidant in DMF at 80 °C for 24 h; however, only a trace amount of the desired product diethyl phenylphosphonate **3aa** was detected (entry 1). No product or only a trace amount of the product was observed when DMSO, CH_3CN or toluene was used as the solvent (entries 2–4). To our delight, when the solvent was changed to ethanol, the coupling product **3aa** was obtained at 22% yield (entry 5). Key role of ethanol in this coupling reaction to obtain the desired product can be explained by the possible coordination of ethanol at boron centre of aryl pinacol boronate. Due to the co-ordination of ethanol with aryl pinacol boronate the electron density at aryl system may be increased. When we chose tetramethylammonium bromide (TMAB), tetramethylammonium chloride (TMAC), LiCl, CsCl and TBACl as the additives, the coupling product **3aa** with TMAC and LiCl obtained 76% and 75% yields, respectively (entries 7 and 9), whereas other additives gave inferior results. To our delight, we chose TMAC as additive for this reaction. Enhancement of the yield of product in the presence of TMAC was because of its phase transfer catalytic and inert counter ionic nature. The yield of the product was decreased to 32% when the reaction was conducted with *tert*-butanol as the solvent (entry 11). The choice of oxidant was crucial in this coupling reaction. When we replaced Ag_2CO_3 with AgOAc and $Cu(OAc)_2$, both led to **3aa** at lower yields (entries 12 and 14); meanwhile, no reaction occurred when $K_2S_2O_8$ or oxygen (ballon) was used as the oxidant (entries 13 and 15). The superiority of Ag_2CO_3 over other oxidants in this reaction could explained by its additional basic nature that can promote the deprotonation of *H*-phosphonates. In the screening of the palladium source, $Pd(PPh_3)_2Cl_2$, $Pd(OCOCF_3)_2$ and $PdCl_2$ showed lower reactivity (entries 16–18) compared with $Pd(OAc)_2$.

We next investigated the relative reactivity of phenyl boronic acid derivatives (Table 2). When phenyl boronic acid (**4**) was used as a boron reagent, the coupling product **3aa** was obtained at 61% yield. Phenyl boronic esters, such as phenyl hexylene glycol boronate (**5**) and phenyl neopentyl glycol boronate (**6**), were also tested, but both gave the product at lower yields when compared with phenyl pinacol boronate (**2a**).

With the optimized protocol from previous works, we examined the scope of the substrates in this catalytic system (Table 3). Various aryl pinacol boronates **2** were found to couple with **1a** to produce the corresponding diethyl arylphosphonates **3** at moderate to good yields. It is worth mentioning that higher yields of products were obtained with aryl pinacol boronates **2** bearing electron-donating groups. Thus, with electron-donating substituents such as methyl and methoxy groups at the C-3 or C-4 position of **2**, one could obtain the corresponding products at good yields (**3aa–3ag**). In contrast, substrates with electron-withdrawing trifluoromethyl and chloro groups led to products at lower yields (**3ah** and **3ai**). When we used 3-bromophenyl

Table 1 Pd-catalyzed coupling of PhB(pin) with diethyl phosphite[a]

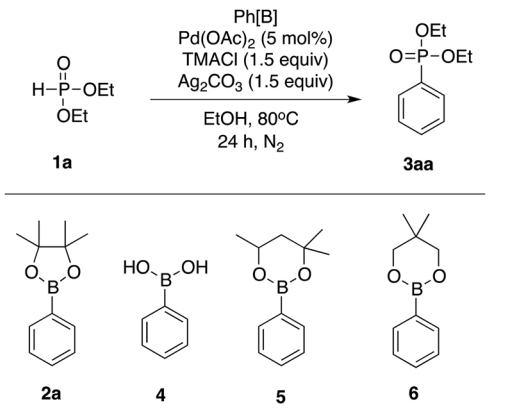


1a 2a 3aa

Entry	Additive	Oxidant	Solvent	Yield[b] (%)
1	—	Ag_2CO_3	DMF	Trace
2	—	Ag_2CO_3	DMSO	0
3	—	Ag_2CO_3	CH_3CN	Trace
4	—	Ag_2CO_3	Toluene	Trace
5	—	Ag_2CO_3	EtOH	22
6	TMAB	Ag_2CO_3	EtOH	25
7	TMAC	Ag_2CO_3	EtOH	76
8	CsCl	Ag_2CO_3	EtOH	50
9	LiCl	Ag_2CO_3	EtOH	75
10	TBAC	Ag_2CO_3	EtOH	35
11	TMAC	Ag_2CO_3	*t*-BuOH	32
12	TMAC	AgOAc	EtOH	35
13	TMAC	$K_2S_2O_8$	EtOH	N.R.
14	TMAC	$Cu(OAc)_2$	EtOH	28
15	TMAC	O_2	EtOH	N.R.
16[c]	TMAC	Ag_2CO_3	EtOH	64
17[d]	TMAC	Ag_2CO_3	EtOH	62
18[e]	TMAC	Ag_2CO_3	EtOH	65

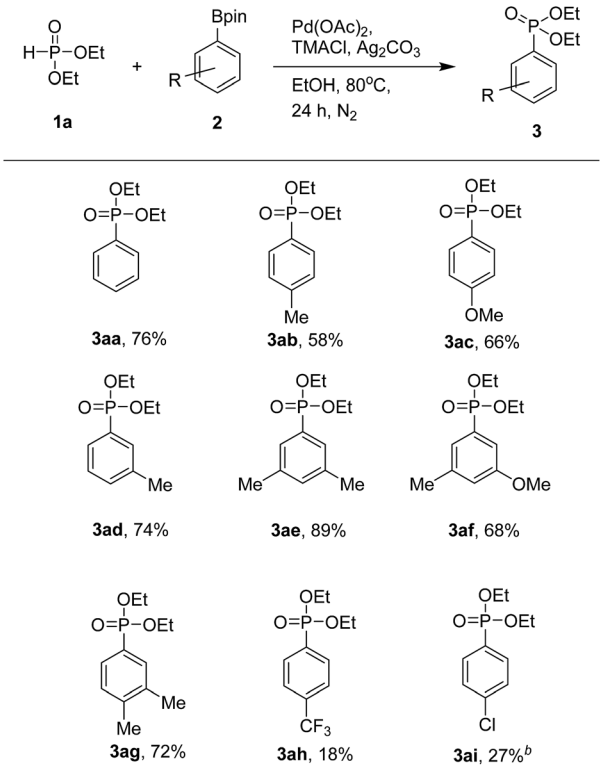
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 eq.), $Pd(OAc)_2$ (5 mol%), additive (1.5 eq.), oxidant (1.5 eq.), and solvent (3.0 mL) under an atmosphere of N_2 for 24 h at 80 °C. [b] Isolated yield. [c] $Pd(PPh_3)_2Cl_2$ as the catalyst. [d] $Pd(OCOCF_3)_2$ as the catalyst. [e] $PdCl_2$ as the catalyst.

Table 2 Phosphorylation: relative reactivity of boron sources[a]



[a] Reaction conditions: 0.5 mmol of **1a**, 1.5 equivalent of Ph[B], 5 mol% $Pd(OAc)_2$, 1.5 equivalent of TMACl, 1.5 equivalent of Ag_2CO_3, and 3 mL of ethanol were charged into a Schlenk tube under nitrogen atmosphere and heated at 80 °C for 24 h.

Table 3 Substrate scope of aryl pinacol boronates[a]



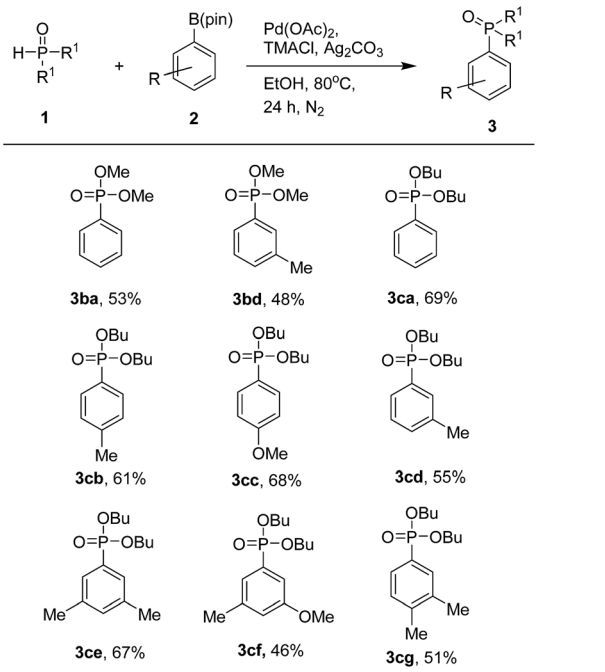
[a] Reaction conditions: 0.5 mmol of **1a**, 1.5 equivalent of boronates **2**, 5 mol% $Pd(OAc)_2$, 1.5 equivalent of TMACl, 1.5 equivalent of Ag_2CO_3, and 3 mL of ethanol were charged into a Schlenk tube under nitrogen atmosphere and heated at 80 °C for 24 h. [b] Reaction at 70 °C.

pinacol boronate as a coupling partner, the desired product was obtained in trace amount along with de-brominated arylphosphonate (**3aa**) in lower yield. Use of various aryl pinacol boronic esters such as 4-nitrophenyl, 4-methoxycarbonylphenyl, 4-cyanophenyl, naphthyl, 4-hydroxyphenyl pinacol boronates and heteroaryl pinacol boronates such as 3-thienyl, 5-indolyl pinacol boronates as substrates to couple with *H*-phosphonate, failed to the formation of desired products instead detected the de-borolyted products. Furthermore, we also tested the reaction by using *ortho* substituted aryl pinacol boronates such as 2-chlorophenyl and mesityl pinacol boronates. Under the reaction conditions, these two substrates also failed to react with *H*-phosphonate. The formation of de-borolyted product was detected by GC analysis. Another important factor that was responsible for lowering the yield of product was formation trialkylphosphates by the reaction of *H*-phosphonate with solvent (ethanol).

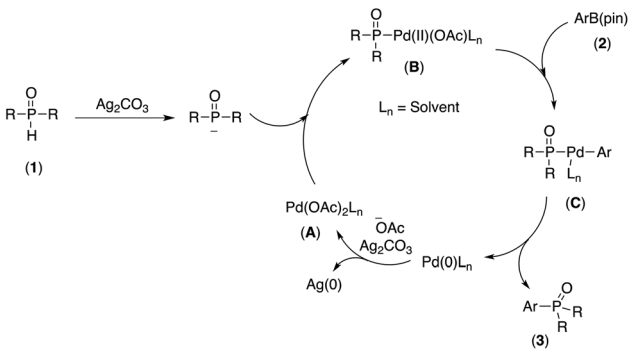
The generality of this coupling reaction was further demonstrated by using two other substituted phosphites, dimethyl phosphite (**1b**) and dibutyl phosphite (**1c**). When screening with different aryl pinacol boronates **2**, both phosphites could produce the corresponding products at moderate to good yields (Table 4).

Although the mechanism of this tranformation is not clear at this stage, based on experimental results, we propose that

Table 4 Pd-catalyzed coupling of aryl pinacol boronates **2** with phosphites[a]



[a] Reaction conditions: 0.5 mmol of **1**, 1.5 equivalent of boronate **2**, 5 mol% $Pd(OAc)_2$, 1.5 equivalent of TMACl, 1.5 equivalent of Ag_2CO_3, and 3 mL of ethanol were charged into a Schlenk tube under nitrogen atmosphere and heated at 80 °C for 24 h.



Scheme 2 Plausible mechanism for the formation of **3**.

this Pd-catalyzed cross-coupling takes place *via* the catalytic cycle shown in Scheme 2. Firstly, the Pd(II) complex **A** reacted with the phosphorous nucleophile generated by deprotonation of the P(O)H compound in the presence of a Ag_2CO_3 to provide intermediate **B**.[22a,d] The resulting intermediate **B** associated with arylpinacol boronate (**2**) to give another intermediate **C**,[22a,d,23] which upon reductive elimination, afforded the desired coupling product (**3**) and Pd(0) species. Finally, the Pd(0) species was oxidized by Ag_2CO_3, leading to the regeneration of Pd(II) complex **A** as a catalytically active species.

Conclusion

In conclusion, we demonstrated a novel Pd-catalyzed cross-coupling reaction of aryl pinacol boronates with *H*-phosphonates, which afforded good yields of arylphosphorus compounds under mild conditions in ethanol. A variety of readily available aryl pinacol boronates can be used in this coupling reaction. We believe that this is a new protocol for the construction of valuable C–P bonds from readily available, environmentally friendly chemical sources.

Experimental

General information

All commercial chemicals were used as received except where noted. Aryl pinacol boronates were all prepared through literature procedures.[24,25] Experiments were performed under a dinitrogen atmosphere using standard Schlenk techniques unless otherwise stated. Flash chromatography was performed on Merck silica gel 60 (230–400 mesh).

Analysis

NMR spectra were recorded on a Varian Unity Inova-600 or a Varian Mercury-400 instrument using $CDCl_3$ as a solvent. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constant (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, quin = quintet, m = multiplet, b = broad. GC-MS analysis were performed on a Agilent Technologies 5977A GC equipped with Agilent 7890B MS. High-resolution mass spectra were carried out on a Jeol JMS-HX 110 spectrometer by the services at the National Chung Hsing University.

General procedure for synthesis of compound 3

To a mixture of aryl pinacol boronic ester (0.75 mmol, 1.5 equiv.), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 1.5 equiv.) and tetramethylammonium chloride (82 mg, 1.5 equiv.) were added *H*-phosphonate (0.5 mmol) and ethanol (3.0 mL) under nitrogen atmosphere. The resulting suspension was heated at 80 °C for 24 h. After 24 h, the reaction mixture was cooled down to room temperature and diluted with ethyl acetate (20 mL). The resulting solution was directly filtered through a pad of celite and the filtrate was concentrated under vacuum. The crude product was purified by flash column chromatography (ethyl acetate/hexane = 30–80/20–70).

Diethyl phenylphosphonate (3aa):.[22] Following the general procedure for compound **3**, using phenylboronic acid pinacol ester **2a** (153 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added diethyl phosphite **1a** (67.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 30–80%) to provide **3aa** as a colorless oil (81.3 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.85 (m, 2H), 7.54–7.58 (m, 1H), 7.45–7.50 (m, 2H), 4.05–4.19 (m, 4H), 1.33 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.3 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 9.9 Hz), 128.4 (d, J_{C-P} = 14.8 Hz), 128.2 (d, J_{C-P} = 186.8 Hz), 62.0 (d, J_{C-P} = 5.3 Hz), 16.2 ((d, J_{C-P} = 6.4 Hz)); ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.54.

Diethyl 4-methylphenylphosphonate (3ab):.[22] Following the general procedure for compound 3, using 4-methylphenylboronic acid pinacol ester (163.6 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added diethyl phosphite **1a** (67.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 30–80%) to provide **3ab** as a colorless oil (66.1 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.26–7.29 (m, 2H), 4.04–4.15 (m, 4H), 2.41 (s, 3H), 1.32 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.92 (d, J_{C-P} = 3.1 Hz), 131.8 (d, J_{C-P} = 10.2 Hz), 129.2 (d, J_{C-P} = 15.5 Hz), 124.8 (d, J_{C-P} = 189.0 Hz), 61.94 (d, J_{C-P} = 5.3 Hz), 21.6 (d, J_{C-P} = 1.2 Hz), 16.26 (d, J_{C-P} = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.21.

Diethyl 4-methoxyphenylphosphonate (3ac):.[22] Following the general procedure for compound 3, using 4-methoxyphenylboronic acid pinacol ester (175.6 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added diethyl phosphite **1a** (67.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 30–80%) to provide **3ac** as a colorless oil (80.5 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 8.8, 1H), 6.95–6.99 (m, 2H), 4.01–4.16 (m, 4H), 3.86 (s, 3H), 1.31 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8 (d, J_{C-P} = 3 Hz), 133.8 (d, J_{C-P} = 11.3 Hz), 119.4 (d, J_{C-P} = 193.5 Hz), 114.0 (d, J_{C-P} = 15.9 Hz), 61.9 (d, J_{C-P} = 4.9 Hz), 55.3, 16.3 (d, J_{C-P} = 6.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.78.

Diethyl 3-methylphenylphosphonate (3ad):.[22] Following the general procedure for compound 3, using 3-methylphenylboronic acid pinacol ester (163.6 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added diethyl phosphite **1a** (67.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 30–80%) to provide **3ad** as a colorless oil (84.4 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.66 (m, 2H), 7.30–7.37 (m, 2H), 4.04–4.18 (m, 4H), 2.40 (s, 3H), 1.33 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2 (d, J_{C-P} = 14.8 Hz), 133.08 (d, J_{C-P} = 3.1 Hz), 132.1 (d, J_{C-P} = 9.8 Hz), 128.5 (d, J_{C-P} = 34.2 Hz), 128.4 (d, J_{C-P} = 40.2 Hz), 127.8 (d, J_{C-P} = 185.9 Hz), 61.9 (d, J_{C-P} = 5.3 Hz), 21.2, 16.2 (d, J_{C-P} = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.91.

Diethyl 3,5-dimethylphenylphosphonate (3ae):.[12] Following the general procedure for compound 3, using 3,5-dimethylphenylboronic acid pinacol ester (174.1 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added diethyl phosphite **1a** (67.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl

acetate/hexane = 30–80%) to provide **3ae** as a colorless oil (107.7 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.41 (s, 1H), 7.18 (s, 1H), 4.03–4.18 (m, 4H), 2.36 (s, 6H), 1.33* (t, J = 7.2 Hz, 3H), 1.32* (t, J = 7.2 Hz, 3H); *This triplet was merged with other triplet; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1 (d, J_{C-P} = 15.6 Hz), 134.1 (d, J_{C-P} = 3.0 Hz), 129.3 (d, J_{C-P} = 9.9 Hz), 127.6 (d, J_{C-P} = 185.2 Hz), 61.9 (d, J_{C-P} = 5.3 Hz), 21.1 (d, J_{C-P} = 1.1 Hz), 16.2 (d, J_{C-P} = 6.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.48.

Diethyl (3-methoxy-5-methylphenyl)phosphonate (3af). Following the general procedure for compound 3, using (3-methoxy-5-methyl)phenyl boronic acid pinacol ester (186.1 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added diethyl phosphite **1a** (67.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 30–80%) to provide **3af** as a colorless oil (87.8 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, J = 13.6 Hz, 1H), 7.13 (d, J = 14.8 Hz, 1H), 6.90 (s, 1H), 4.18–4.04 (m, 4H), 3.82 (s, 3H), 2.37 (s, 3H), 1.33 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3 (d, J_{C-P} = 20.1 Hz), 140.0 (d, J_{C-P} = 17.9 Hz), 128.9 (d, J_{C-P} = 185.2 Hz), 124.7 (d, J_{C-P} = 9.5 Hz), 119.4 (d, J_{C-P} = 3.0 Hz), 113.2 (d, J_{C-P} = 11.4 Hz), 62.0 (d, J_{C-P} = 4.9 Hz), 55.3, 21.3, 16.24 (d, J_{C-P} = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.98; HRMS-EI calcd for $C_{12}H_{19}O_4P$ $[M]^+$: 258.1021, found: 258.1028.

Diethyl 3,4-dimethylphenylphosphonate (3ag):.[11] Following the general procedure for compound 3, using 3,4-dimethylphenylboronic acid pinacol ester (174.1 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added diethyl phosphite **1a** (67.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 30–80%) to provide **3ag** as a colorless oil (87.2 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.61 (m, 2H), 7.21–7.28 (m, 1H), 4.02–4.17 (m 4H), 2.31 (s, 6H), 1.33 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7 (d, J_{C-P} = 3.4 Hz), 137.0 (d, J_{C-P} = 15.2 Hz), 132.8 (d, J_{C-P} = 10.3 Hz), 129.6 (d, J_{C-P} = 45.9 Hz), 129.5 (d, J_{C-P} = 40.2 Hz), 125.1 (d, J_{C-P} = 187.8 Hz), 61.9 (d, J_{C-P} = 5.3 Hz), 19.9, 19.6, 16.3 (d, J_{C-P} = 6.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.59.

Diethyl 4-trifluoromethylmethylphenylphosphonate (3ah):.[22] Following the general procedure for compound 3, using 4-trifluorophenylboronic acid pinacol ester (204.1 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added diethyl phosphite **1a** (67.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 30–80%) to provide **3ah** as a colorless oil (25.4 mg, 18% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, J = 7.6 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.72–7.75 (m, 2H), 4.10–4.20 (m, 4H), 1.34 (t, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.0 (d, J = 33.0 Hz), 132.7 (d, J = 185.5 Hz), 132.2 (d, J = 9.9 Hz), 125.3 (dq, J = 15.1, 3.8 Hz), 123.5 (q, J = 270.6 Hz), 62.5 (d, J = 5.7 Hz), 16.3 (d, J = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.02; ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.3.

Diethyl 4-chlorophenylphosphonate (3ai):.[12] Following the general procedure for compound 3, using 4-chlorophenylboronic acid pinacol ester (178.6 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added diethyl phosphite **1a** (67.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 30–80%) to provide **3ai** as a colorless oil (33.5 mg, 27% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.4 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.44–7.47 (m, 2H), 4.04–4.19 (m, 4H), 1.33 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9 (d, J_{C-P} = 3.8 Hz), 133.2 (d, J_{C-P} = 10.7 Hz), 128.8 (d, J_{C-P} = 15.6 Hz), 126.9 (d, J_{C-P} = 190.1 Hz), 62.25 (d, J_{C-P} = 5.7 Hz), 16.3 (d, J_{C-P} = 6.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 18.67.

Dimethyl phenylphosphonate (3ba):.[22] Following the general procedure for compound 3, using phenylboronic acid pinacol ester (153 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added dimethyl phosphite (46.7 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 30–80%) to provide **3ba** as a colorless oil (49.3 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78–7.84 (m, 2H), 7.56–7.60 (m, 1H), 7.46–7.51 (m, 2H), 3.78 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.6 (d, J_{C-P} = 3.0 Hz), 131.8 (d, J_{C-P} = 9.9 Hz), 128.5 (d, J_{C-P} = 15.2 Hz), 126.8 (d, J_{C-P} = 187.8 Hz), 52.6 (d, J_{C-P} = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.33.

Dimethyl 3-methylphenylphosphonate (3bd). Following the general procedure for compound 3, using 3-methylphenylboronic acid pinacol ester (163.6 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added dimethyl phosphite (46.7 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 30–80%) to provide **3bd** as a colorless oil (48.0 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.65 (m, 2H), 7.38 (b, 2H), 3.73–3.78 (m, 6H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4 (d, J_{C-P} = 15.2 Hz), 133.4 (d, J_{C-P} = 3.1 Hz), 132.3 (d, J_{C-P} = 9.8 Hz), 128.7 (d, J_{C-P} = 39.1 Hz), 128.6 (d, J_{C-P} = 45.5 Hz), 126.5 (d, J_{C-P} = 186.7 Hz), 52.6 (d, J_{C-P} = 5.3 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.80; HRMS-EI calcd for $C_9H_{13}O_3P$ $[M]^+$: 200.0602, found: 200.0597.

Dibutyl phenylphosphonate (3ca):.[11] Following the general procedure for compound 3, using phenylboronic acid pinacol ester **2a** (153 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added dibutyl phosphite (101.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 20–70%) to provide **3ca** as a colorless oil (93.2 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.84 (m, 2H), 7.53–7.58 (m, 1H), 7.44–7.49 (m, 2H), 3.96–4.12 (m, 4H), 1.61–1.69 (m, 4H), 1.34–1.44 (m, 4H), 0.90 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.3, 131.7 (d, J_{C-P} = 9.1 Hz), 128.4 (d, J_{C-P} = 14.5 Hz), 128.3 (d, J_{C-P} = 186.6 Hz), 65.7 (d, J_{C-P} = 5.4 Hz), 32.4 (d, J_{C-P} = 6.4 Hz), 18.7, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.36.

Dibutyl *p*-tolylphosphonate (3cb):.[15] Following the general procedure for compound 3, using *p*-tolylphenylboronic acid pinacol ester (163.6 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added dibutyl phosphite (101.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 20–70%) to provide **3cb** as a colorless oil (86.7 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.25–7.29 (m, 2H), 3.96–4.09 (m, 4H), 2.40 (s, 3H), 1.65 (quin, J = 6.8 Hz, 4H), 1.34–1.44 (m, 4H), 0.90 (t, J = 7.2, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7 (d, J_{C-P} = 2.3 Hz), 131.6 (d, J_{C-P} = 10.2 Hz), 129.0 (d, J_{C-P} = 15.2 Hz), 124.7 (d, J_{C-P} = 189.4 Hz), 65.5 (d, J_{C-P} = 5.7 Hz), 32.2 (d, J_{C-P} = 6.5 Hz), 21.4, 18.5, 13.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.09.

Dibutyl 4-methoxyphenylphosphonate (3cc):.[26] Following the general procedure for compound 3, using 4-methoxyphenylboronic acid pinacol ester (175.6 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added dibutyl phosphite (101.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 20–70%) to provide **3cc** as a colorless oil (102.1 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 6.95–6.99 (m, 2H), 3.94–4.07 (m, 4H), 3.85 (s, 3H), 1.60–1.68 (m, 4H), 1.35–1.44 (m, 4H), 0.90 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, J_{C-P} = 2.8 Hz), 133.6 (d, J_{C-P} = 10.9 Hz), 119.3 (d, J_{C-P} = 192.9 Hz), 113.8 (d, J_{C-P} = 15.4 Hz), 65.5 (d, J_{C-P} = 5.4 Hz), 55.1, 32.3 (d, J_{C-P} = 6.3 Hz), 18.6, 13.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.47; HRMS-EI calcd for $C_{15}H_{25}O_4P$ $[M]^+$: 300.1490, found: 300.1484.

Dibutyl 3-methylphenylphosphonate (3cd). Following the general procedure for compound 3, using 3-methylphenylboronic acid pinacol ester (163.6 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added dibutyl phosphite (101.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 20–70%) to provide **3cd** as a colorless oil (78.1 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.65 (m, 2H), 7.34–7.37 (m, 2H), 3.95–4.11 (m, 4H), 2.40 (s, 3H), 1.62–1.70 (m, 4H), 1.34–1.45 (m, 4H), 0.91 (t, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.1 (d, J_{C-P} = 14.5 Hz), 133.0, 132.2 (d, J_{C-P} = 10 Hz), 128.5 (d, J_{C-P} = 40 Hz), 128.4 (d, J_{C-P} = 46.4 Hz), 128.0 (d, J_{C-P} = 187.5 Hz), 65.6 (d, J_{C-P} = 5.5 Hz), 32.3 (d, J_{C-P} = 7.3 Hz), 21.2, 18.6, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.91; HRMS-EI calcd for $C_{15}H_{25}O_3P$ $[M]^+$: 284.1541, found: 284.1540.

Dibutyl 3,5-dimethylphenylphosphonate (3ce). Following the general procedure for compound 3, using 3,5-dimethylphenylboronic acid pinacol ester (174.1 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added dibutyl phosphite (101.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 20–70%) to provide **3ce** as a colorless oil (99.8 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1H), 7.39 (s, 1H), 7.17 (s, 1H), 3.96–4.09 (m, 4H), 2.35 (s, 6H), 1.62–1.70 (m, 4H), 1.36–1.43 (m, 4H), 0.91 (t, J = 7.2, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0 (d, J_{C-P} = 15.4 Hz), 133.95 (d, J_{C-P} = 2.7 Hz), 129.3 (d, J_{C-P} = 10 Hz), 127.8 (d, J_{C-P} = 184.8 Hz), 65.6 (d, J_{C-P} = 5.5 Hz), 32.4 (d, J_{C-P} = 7.3 Hz), 21.1, 18.6, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.40; HRMS-EI calcd for $C_{16}H_{27}O_3P$ $[M]^+$: 298.1698, found: 298.1707.

Dibutyl (3-methoxy-5-methylphenyl)phosphonate (3cf). Following the general procedure for compound 3, using (3-methoxy-5-methyl)phenyl boronic acid pinacol ester (186.1 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added dibutyl phosphite (101.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 20–70%) to provide **3cf** as a colorless oil (72.3 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10–7.23 (m, 2H), 6.89 (s, 1H), 3.97–4.10 (m, 4H), 3.82 (s, 3H), 2.37 (s, 3H), 1.62–1.70 (m, 4H), 1.35–1.45 (m, 4H), 0.91 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4 (d, J_{C-P} = 19.8 Hz), 139.9 (d, J_{C-P} = 17.4 Hz), 129.0 (d, J_{C-P} = 185.2 Hz), 124.7 (d, J_{C-P} = 9.5 Hz), 119.4 (d, J_{C-P} = 3.4 Hz), 113.3 (d, J_{C-P} = 11 Hz), 65.75 (d, J_{C-P} = 5.7 Hz), 55.3, 32.4 (d, J_{C-P} = 6.5 Hz), 21.31 (d, J_{C-P} = 1.5 Hz), 18.7, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.69; HRMS-EI calcd for $C_{16}H_{27}O_4P$ $[M]^+$: 314.1647, found: 314.1655.

Dibutyl 3,4-dimethylphenylphosphonate (3cg). Following the general procedure for compound 3, using 3,4-dimethylphenylboronic acid pinacol ester (174.1 mg, 0.75 mmol), $Pd(OAc)_2$ (5.6 mg, 5 mol%), Ag_2CO_3 (0.21 g, 0.75 mmol) and tetramethylammonium chloride (82 mg, 0.75 mmol) were added dibutyl phosphite (101.5 μL, 0.50 mmol) in ethanol (3.0 mL), then purified by column chromatography (SiO_2, ethyl acetate/hexane = 20–70%) to provide **3cg** as a colorless oil (76.0 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.59 (m, 2H), 7.20–7.24 (m, 1H), 3.93–4.10 (m, 4H), 2.30 (s, 6H), 1.61–1.69 (m, 4H), 1.34–1.44 (m, 4H), 0.91 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 136.9 (d, J_{C-P} = 15.4 Hz), 132.8 (d, J_{C-P} = 10.0 Hz), 129.6 (d, J_{C-P} = 43.7 Hz), 129.4 (d, J_{C-P} = 38.2 Hz), 125.2 (d, J_{C-P} = 188.4 Hz), 65.6 (d, J_{C-P} = 6.4 Hz), 32.4 (d, J_{C-P} = 7.3 Hz), 19.9, 19.6, 18.7, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 20.51; HRMS-EI calcd for $C_{16}H_{27}O_3P$ $[M]^+$: 298.1698, found: 298.1700.

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