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Copper-Catalyzed P-Arylation via Direct Coupling of Diaryliodonium Salts with Phosphorus Nucleophiles at Room Temperature

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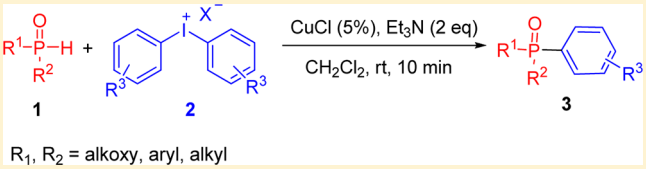
Supporting Information

ABSTRACT: A new method for copper-catalyzed P−C bond formation through reaction of phosphorus nucleophiles with diaryliodonium salts at room temperature is described. Most target products are obtained with this method in high yields within a short reaction time of 10 min. It can be easily adapted to large-scale preparations. When unsymmetrical iodonium salts are employed, nucleophilic substitution occurs preferentially on the sterically hindered aromatic ring or the more electron-deficient ring.



Aromatic phosphorus compounds have broad applications in medicinal chemistry[1] and photoelectric materials[2,3] and act as excellent ligands in transition-metal catalysis.[4,5] The traditional methods for their preparations rely on the reaction of organometallic reagents with $Ph_2P(O)Cl$. In 1980, Hirao et al. reported the pioneering work of palladium-catalyzed phosphonation of aryl iodides or bromides.[6] The first phosphonation of aryl iodides and bromides with diphenylphosphine oxide in neat water was reported by our group using $NiCl_2$/zinc powder as the catalyst in 2011.[7] Very recently, Bokhoven and Wu's group also described cross-coupling of halogenated benzene with diphenylphosphine oxide or *H*-phosphonate using Pd as the catalyst in water.[8,9] Over the past decade, different aryl substances were investigated for their reactivity with phosphorus nucleophiles. Since 2009, Larhed et al. and our group have developed the Cu- and Pd-catalyzed coupling of arylboronic acids or aryl trifluoroborates with *H*-phosphonate.[10,11] Reaction of an aryl imidazolylsulfonate with an *H*-phosphonate was reported by Wu and Luo in 2009.[12] Synthesis of arylphosphonates from arenediazonium tetrafluoroborates and triethylphosphite or diethylphosphite was presented by Cacchi's group in 2010.[13] The utilization of phenolic esters in arylphosphonate preparations was studied in 1987 by Lu's group[14] and Petrakis's group[15] and also explored by Zhang's group in 2012.[16] Direct oxidative phosphonation of benzene derivatives and azoles was also reported in recent years.[17−19] However, these methods have some significant drawbacks, such as the requirement of a noble catalyst, long reaction time, and low yield for bulky substrates, which likely limit their application in organic synthesis. Consequently, development of a new method to circumvent these limitations is highly desirable.

Diaryliodonium salts, as important and valuable electrophilic arylation reagents, have attracted much attention in recent years due to their high reactivity and nontoxicity. They serve as powerful arylating agents in transition-metal-catalyzed direct C−H bond arylations;[20−22] coupling reagants in Suzuki,[23] Sonogashira,[24] and Heck reactions;[25] and also in reactions with a variety of nucleophiles under metal-free or other metal-catalyzed conditions.[26−33] The stereoselective preparation of 2-arylvinylphosphonates using vinyliodonium tetrafluoroborates was discovered by Bisseret et al. in 2005.[34] Moreover, owing to the efforts of Beringer, Olofsson, and others, these compounds can now be easily prepared in one pot.[35−41]

On the basis of the above reports, we were interested in diaryliodonium salts as potential arylating agents for phosphorus nucleophiles.

To test this hypothesis, diphenylphosphine oxide (**1a**) and diphenyliodonium triflate (**2a**) were used as model substrates for optimization of reaction conditions. At the outset, the reaction was carried out under metal-free conditions for 24 h; however, only a trace amount of product **3a** was detected. A similar result was obtained when $Pd(OAc)_2$ was employed as a catalyst. Surprisingly, when 5 mol % of $Cu(OAc)_2$ and 2.0 equiv of Et_3N were used as the catalyst and base, the desired target product **3a** was formed in a yield of 80% within 10 min (Table 1, entry 3, ^{31}P NMR yield). Subsequently, various copper salts were screened under similar conditions, of which CuCl showed the highest activity and efficacy, whereas other tested salts, CuI, CuO, $CuSO_4$, $Cu(OTf)_2$, and $CuCl_2$, were less effective (entries 3−11). In addition to Et_3N, other tested bases, such as *i*-Pr_2NEt, *t*-BuOK, and Cs_2CO_3, all gave good yields. However, pyridine, a weak organic base, resulted in a very low yield. The effect of the solvents was also investigated, and CH_2Cl_2 was found to be the most suitable solvent. The reaction could give

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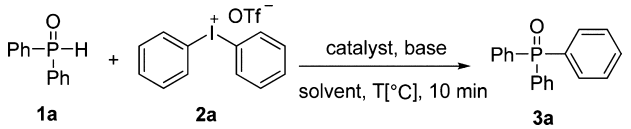
Table 1. Optimization of Reaction Conditions[a]



1a 2a 3a

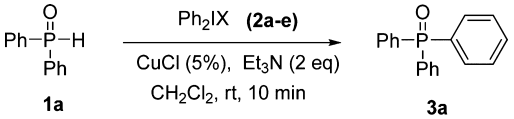
entry	catalyst	base	solvent	T (°C)	yield (%)
1		*t*-BuOK	DMF	110	trace
2	$Pd(OAc)_2$	Et_3N	DMF	110	trace
3	$Cu(OAc)_2$	Et_3N	DMF	110	80
4	$Cu(OTf)_2$	Et_3N	DMF	110	82
5	$CuSO_4$	Et_3N	DMF	110	71
6	$CuCl_2$	Et_3N	DMF	110	83
7	CuBr	Et_3N	DMF	110	85
8	CuI	Et_3N	DMF	110	87
9	**CuCl**	**Et_3N**	**DMF**	**110**	**92**
10	CuO	Et_3N	DMF	110	18
11	$Cu(acac)_2$	Et_3N	DMF	110	37
12	CuCl	*t*-BuOK	DMF	110	88
13	CuCl	DBU	DMF	110	91
14	CuCl	Pyr	DMF	110	trace
15	CuCl	Cs_2CO_3	DMF	110	70
16	CuCl	*i*-Pr_2NEt	DMF	110	86
17	CuCl	Et_3N	toluene	110	92
18	CuCl	Et_3N	dioxane	100	90
19	CuCl	Et_3N	DMSO	50	86
20	**CuCl**	**Et_3N**	**CH_2Cl_2**	**50**	**98**
21	CuCl	Et_3N	CH_3CN	80	76
22	CuCl	Et_3N	DCE	70	86
23	CuCl	Et_3N	THF	60	82
24[b]	**CuCl**	**Et_3N**	**CH_2Cl_2**	**rt**	**97**
25	CuCl	Et_3N	CH_2Cl_2	0	97
26		Et_3N	CH_2Cl_2	rt	trace
27	CuCl	Et_3N-TEMPO	CH_2Cl_2	rt	0

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.5 mmol), base (1.0 mmol), and solvent (1.5 mL), under air for 10 min in a sealed tube. Yields were determined by ^{31}P NMR. [b]Air or nitrogen condition gave the same yield.

an almost quantitative conversion in a broad temperature range (0–110 °C) (entries 9, 20, 24, 25). Even at room temperature, a 97% yield was obtained within 10 min. However, no desired product was obtained when 1.0 equiv of TEMPO was added into the reaction according to the optimal conditions (entry 27). It was suggested that diphenyliodonium salt would convert into triphenylphosphine oxide via a radical pathway.[20,42]

Having the optimal condition in hand, we turned our attention to examining the effect of counterions in this reaction (Table 2). No significant differences in yield of **3a** were observed among the anions OTf (97%), BF_4 (95%), PF_6 (93%), and OTs (90%). However, the bromide anion is more nucleophilic and is in competition with diphenylphosphine oxide, therefore, giving the desired product in a slightly lower yield.[43]

Table 2. Effect of the Counteranions



1a 3a

entry		X	yields (%, ^{31}PNMR)
1	**2a**	OTf	97
2	**2b**	BF_4	95
3	**2c**	PF_6	93
4	**2d**	OTs	90
5	**2e**	Br	80

The reaction scope was subsequently explored with diarylphosphine oxide and various substituted symmetrical diaryliodoniums (Table 3). Triarylphosphine oxides were obtained in 91–98% yields (**3a–3f**) when diphenylphosphine oxide reacted with diaryliodonium triflates (**2a**, **2f–2j**) at room temperature. When diaryliodonium tetrafluoroborates (**2k–2o**) were used, the products were formed in 72–90% yields (**3g–3k**). The use of diaryliodonium bromides (**2p**, **2q**) led to slightly lower yields (**3l**, **3m**). 4-Fluoro-, 4-chloro-, and 4-bromodiphenyliodonium triflates (**2f–2h**) were also examined for their reactivity with diphenylphosphine oxide under similar reaction conditions to give the expected products **3b–3d** in 91–96% yields. Symmetrical iodonium salts with electron-donating (phenyl and methoxy) or electron-withdrawing (CF_3, NO_2, and COOH) groups all produced the desired products in good yields, suggesting that the substituted groups did not have a significant influence on the reaction. Gratifyingly, steric bulk posed no problem in this reaction, as exemplified by the high yield of the ortho-Me product **3g** obtained. Remarkably, the sterically hindered 2,4,6-tri-Me-Ph could be transferred and gave **3f** in nearly quantitative yield.

A series of substituted diphenylphosphine oxides were tested under the optimized reaction conditions subsequently (Table 3). Diverse functional groups, including Cl, F, OMe, dimethyl amino, and acetals, could be tolerated; corresponding products were obtained in high yields (**3o–3v**). Phenylethylphosphine oxide was also tested for this reaction, affording the corresponding product **3w** in 94% yield. Dialkylphosphine oxide with a long and bulky aliphatic chain was arylated to give the product **3x** in moderate yield.

With regards to the *H*-phosphonates, dimethyl (**1b**), diethyl (**1c**), and dibenzyl *H*-phosphate (**1d**) all could be used as the substrates, generating the corresponding arylphosphonates (**4a–4f**) in 78–95% yields (Table 4). *H*-Phosphonate containing double bonds reacted smoothly with iodonium salt to give **4g** in 93% yield. Treatment of ethyl phenylphosphinate (**1f**) with iodonium salt led to the formation of product **4h** in high yield.

Thereafter, the regioselectivity of unsymmetrical diaryliodonium salts **5** was investigated through the use of ^{31}P NMR (Table 5). Previous reports indicate that less bulky aryl groups are transferred more readily than bulky aryl groups, and electron-rich functionalities are transferred prefentially over electron-deficient functionalities under metal-catalyzed reactions.[32,44] Interestingly, contrasting selectivities were observed in our reactions. When unsymmetrical systems were employed, observations suggested that nucleophilic substitution occurred preferentially on the sterically demanding aromatic ring or the more electron-deficient ring.

When phenyl(2,4,6-triisopropylphenyl)iodonium salt (**5c**) was used, steric control resulted in substitution of the hindered 2,4,6-triisopropylphenyl ring as the only product (Table 5, entry 3, **3z**). Substituted phenyl ring with electron-donating *p*-methoxy and the other ring with electron-withdrawing *p*-nitrol groups of the salt (**5f**) reacted with diphenylphosphine oxide to result in substitution of the electron-deficient ring as the major product (Table 5, entry 6, **4i**, **3i**). The above results highlight such selectivity. This opposite regioselectivity may be due to

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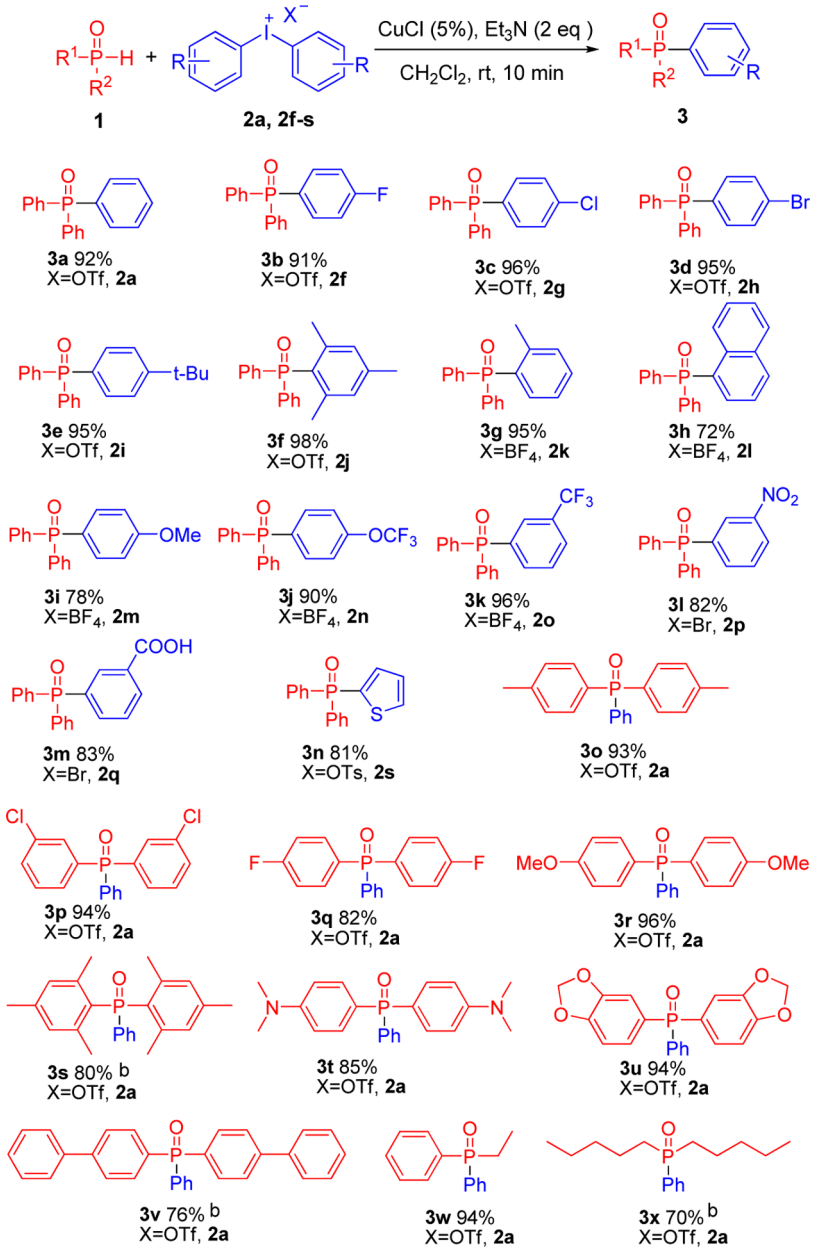
Table 3. Copper-Catalyzed Coupling of Symmetrical Iodonium Salts with Diarylphosphine Oxides[a,b]



[a]Reaction conditions: **1** (0.6 mmol), **2a–2s** (0.5 mmol), and Et_3N (1.0 mmol) in CH_2Cl_2 (1.5 mL) at r.t for 10 min. [b]4 h needed.

the difference in mechanism. Our copper-catalyzed reaction involved a radical mechanism that was inconsistent with the previous Cu(III)-intermediate mechanism.[44] In a radical mechanism, the phenyl radical with a sterically demanding or electron-deficient group is more stable, and thus transfer to the corresponding product in high regioselectivity.

Finally, in order to demonstrate the practical application of this method, diaryliodo salt **2g** (20 mmol) was employed in a large-scale reaction with **1a** (24 mmol) and delivered **3c** in 94% yield. The byproduct 1-chloro-4-iodobenzene was recovered in 95% yield. It is noteworthy that decreasing the catalytic loading to 0.5 mol % of CuCl still gave **3c** in 90% yield, albeit after a longer reaction time of 20 h (Scheme 1).

In summary, we have demonstrated a fast, high-yielding, and scalable system for the arylation of *H*-phosphonates and diarylphosphine oxide with symmetrical and unsymmetrical diaryliodonium salts catalyzed by copper(I) chloride. This method avoids using any air-sensitive reagents, and the reaction can, therefore, be performed under ambient conditions, rendering the experimental procedure very simple. Moreover, the diaryliodonium salts can be readily prepared from the corresponding arene compounds. Therefore, this synthetic method potentially has wide application for the construction of biologically active molecules, catalytic ligands, and organophosphorus compounds.

EXPERIMENTAL SECTION

General. All reactions were carried out under ambient conditions. All reagents were purchased and used without further purification. The solvent was freshly distilled. All new compounds were further characterized by HRMS(FT-ICR-MS).

General Procedure for the Coupling of Diaryliodonium Salts with H(O)PR_1R_2. A 10 mL Schlenk tube was charged with CuCl (5.0 mg, 5 mol %), diaryliodonium salt **2** or **5** (0.50 mmol), CH_2Cl_2 (1.5

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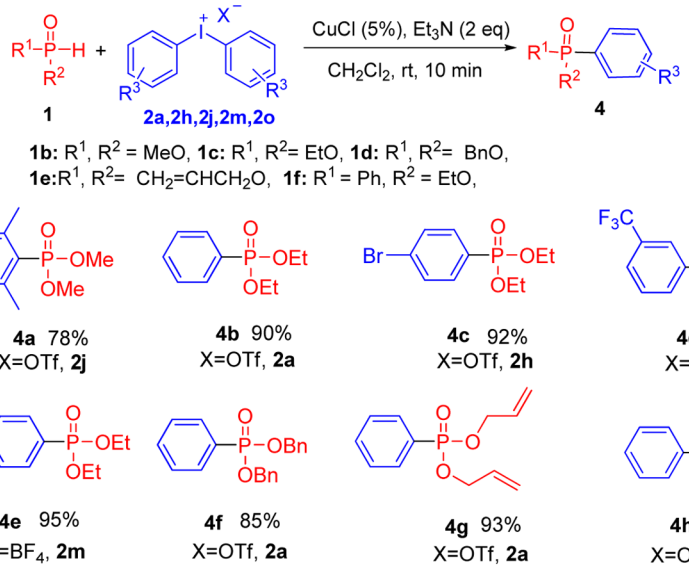
Table 4. Arylation of *H*-Phosphonates with Symmetrical Iodonium Salts[a]



[a]Reaction conditions: **1** (0.6 mmol), symmetrical iodonium salts (0.5 mmol), and Et_3N (1.0 mmol) in CH_2Cl_2 (1.5 mL) at r.t for 10 min.

mL), and Et_3N (101 mg, 1.0 mmol), and the reaction mixture was stirred at r.t., followed by dropwise addition of $H(O)PR_1R_2$ **1** (0.60 mmol). After 10 min, the crude reaction mixture was purified by flash chromatography using petroleum−AcOEt (2:1, v/v) as the eluent to give triarylphosphine oxide **3** or **4**.

The preparations of symmetrical and unsymmetrical iodonium salts are shown in refs 38 and 41, respectively.

*Triphenylphosphine Oxide (**3a**) (CAS no: 791-28-6).* White solid; 128 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.61 (m, 6 H), 7.51−7.47 (m, 3 H), 7.43−7.39 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.0, 132.1 (d, J = 10.0 Hz), 131.9 (d, J = 2.8 Hz), 128.5 (d, J = 11.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.0. MS-ESI: m/z 279.1, $[M + H]^+$.

*(4-Fluorophenyl)diphenylphosphine Oxide (**3b**) (CAS no: 18437-73-5).* White solid; 134 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 7.67−7.60 (m, 6 H), 7.53−7.49 (m, 2 H), 7.44−7.41 (m, 4 H), 7.11 (t, J = 8.5 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0 (dd, J = 254.2, 3.2 Hz), 134.6 (dd, J = 11.3, 8.9 Hz), 132.5 (d, J = 105.2 Hz), 132.1 (d, J = 4.1 Hz), 132.0, 128.7 (dd, J = 106.6, 3.1 Hz), 128.6 (d, J = 12.5 Hz), 115.9 (dd, J = 22.6, 13.3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 28.32. MS-ESI: m/z 297.1, $[M + H]^+$.

*(4-Chlorophenyl)diphenylphosphine Oxide (**3c**) (CAS no: 34303-18-9).* White solid; 150 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.59 (m, 6 H), 7.53−7.50 (m, 2 H), 7.45−7.42 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2 (d, J = 3.2 Hz), 133.2 (d, J = 11.0 Hz), 131.9 (d, J = 2.7 Hz), 131.7 (d, J = 105.6 Hz), 131.6 (d, J = 9.7 Hz), 130.8 (d, J = 105.2 Hz), 128.6 (d, J = 12.4 Hz), 128.4 (d, J = 12.3 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 28.2. MS-ESI: m/z 313.1, $[M + H]^+$.

*(4-Bromophenyl)diphenylphosphine Oxide (**3d**) (CAS no: 5525-40-6).* Colorless oil; 169 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.62 (m, 3 H), 7.61−7.56 (m, 3 H), 7.55−7.49 (m, 4 H), 7.46−7.42 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.6 (d, J = 10.3 Hz), 132.2 (d, J = 2.7 Hz), 132.1 (d, J = 105.0 Hz), 132.0 (d, J = 10.2 Hz), 131.9 (d, J = 12.4 Hz), 131.8 (d, J = 104.0 Hz), 128.7 (d, J = 12.4 Hz), 127.2 (d, J = 2.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.9. MS-ESI: m/z 357.1, $[M+H]^+$.

*(4-(tert-Butyl)phenyl)diphenylphosphine Oxide (**3e**).* White solid; mp 132−133 °C; 159 mg, 95% yield. IR (film): 3449, 3020, 1600, 1398, 1181, 1114, 806, 658. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58−7.49 (m, 6 H), 7.37−7.30 (m, 8 H), 1.20 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 132.5 (d, J = 104.5 Hz), 131.7 (d, J = 9.7 Hz), 131.6 (d, J = 10.3 Hz), 131.5 (d, J = 2.0 Hz), 129.0 (d, J = 107.2 Hz), 128.2 (d, J = 12.1 Hz), 125.2 (d, J = 12.5 Hz), 34.7, 30.8. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.6. HRMS-ESI: calcd for $C_{22}H_{23}OP(M + K)^+$, 373.1123; found, 373.1121.

*Mesityldiphenylphosphine Oxide (**3f**) (CAS no: 91239-43-9).* White solid; 157 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.61 (m, 4 H), 7.51−7.46 (m, 2 H), 7.44−7.39 (m, 4 H), 6.87 (d, J = 3.8 Hz, 2 H), 2.28 (s, 3 H), 2.10 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5 (d, J = 9.9 Hz), 141.8 (d, J = 2.5 Hz), 135.8 (d, J = 102.9 Hz), 131.6 (d, J = 10.3 Hz), 131.5 (d, J = 2.5 Hz), 131.2 (d, J = 11.3 Hz), 128.7 (d, J = 12.5 Hz), 125.6 (d, J = 102.5 Hz), 24.1 (d, J = 4.4 Hz), 21.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.4. MS-ESI: m/z 321.2, $[M + H]^+$.

*Diphenyl(o-tolyl)phosphine Oxide (**3g**) (CAS no: 6840-26-2).* Light yellow solid; 139 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.61 (m, 4 H), 7.53−7.49 (m, 2 H), 7.46−7.37 (m, 5 H), 7.28−7.24 (m, 1H), 7.12−7.08 (m, 1 H), 7.04−6.99 (m, 1 H), 2.44 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2 (d, J = 8.2 Hz), 133.4 (d, J = 13.0 Hz), 132.7 (d, J = 103.2 Hz), 132.0 (d, J = 2.8 Hz), 131.9, 131.8, 131.7 (d, J = 2.7 Hz), 130.7 (d, J = 102.7 Hz), 128.5 (d, J = 11.8 Hz), 125.2 (d, J = 12.6 Hz), 21.6 (d, J = 5.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.7. MS-ESI: m/z 293.1, $[M + H]^+$.

*Naphthalen-1-yldiphenylphosphine Oxide (**3h**) (CAS no: 3095-33-8).* Black solid; 118 mg, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (d, J = 8.3 Hz, 1 H), 8.01 (d, J = 8.4 Hz, 1 H), 7.88 (d, J = 7.8 Hz, 1 H), 7.72−7.68 (m, 4 H), 7.54−7.28 (m, 10 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.9, 133.8 (d, J = 10.1 Hz), 133.7,133.4, 132.1 (d, J = 10.2 Hz), 131.9, 128.8, 128.6 (d, J = 12.0 Hz), 127.6 (d, J = 6.1 Hz), 127.4, 126.5, 124.2 (d, J = 15.2). ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.4. MS-ESI: m/z 329.1, $[M + H]^+$.

*(4-Methoxyphenyl)diphenylphosphine Oxide (**3i**) (CAS no: 795-44-8).* Yellow oil; 120 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67−7.61 (m, 4 H), 7.59−7.48 (m, 4 H), 7.44−7.40 (m, 4 H), 6.96−6.93 (m, 2 H), 3.81 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.5 (d, J = 2.8 Hz), 134.0 (d, J = 11.3 Hz), 133.0 (d, J = 104.5 Hz), 132.1 (d, J = 9.6 Hz), 131.9 (d, J = 2.4 Hz), 128.5 (d, J = 12.4 Hz), 124.1 (d, J = 107.3 Hz), 114.2 (d, J = 13.1 Hz), 55.4. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.1. MS-ESI: m/z 309.1, $[M + H]^+$.

*Diphenyl(4-(trifluoromethoxy)phenyl)phosphine Oxide (**3j**).* Colorless oil; 163 mg, 90% yield. IR (film): 3447, 3058, 1596, 1493, 1437, 1118, 723. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75−7.64 (m, 6 H), 7.58−7.54 (m, 2 H), 7.49−7.47 (m, 4 H), 7.30 (d, J = 8.4 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 134.1 (d, J = 11.1 Hz), 132.3 (d, J = 2.4 Hz), 132.2 (d, J = 10.1 Hz), 132.1 (d, J = 105.4 Hz), 130.9, 128.7 (d, J = 12.3 Hz), 120.6 (d, J = 13.1 Hz), 120.4 (d, J = 259.9 Hz).

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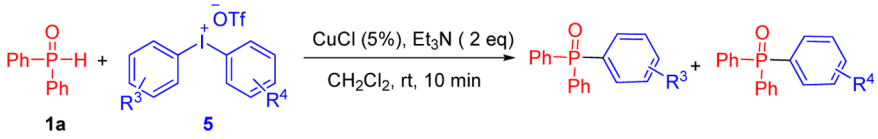
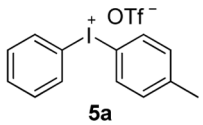
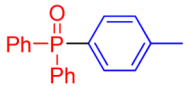
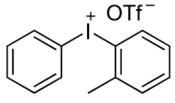
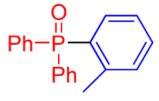
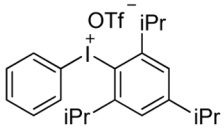
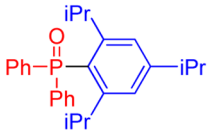
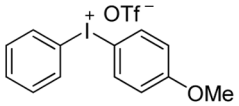
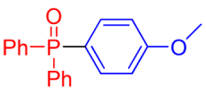
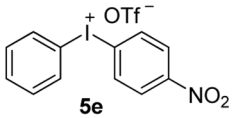
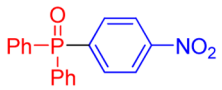
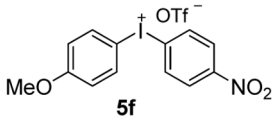
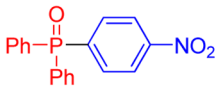
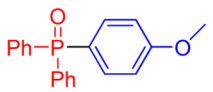
Table 5. Arylation of Diphenylphosphine Oxide with Unsymmetrical Iodonium Salts[a,b]

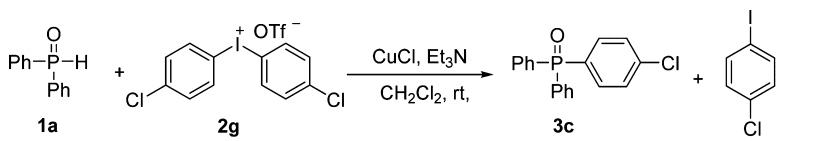


1a 5

entry	salt	product		ratio[b]	yield (%)
1	 5a	 3y	Ph_3PO 3d	1:1	97
2	 5b	 3g	Ph_3PO 3d	2:1	96
3	 5c	 3z		–	99
4	 5d	 3i	Ph_3PO 3d	1:2.4	94
5	 5e	 4i	Ph_3PO 3d	4:1	90
6	 5f	 4i  3i		14:1	88

[a]Reaction conditions: **1** (0.6 mmol), **5** (0.5 mmol), and Et_3N (1.0 mmol) in CH_2Cl_2 (1.5 mL) at r.t for 10 min. [b]The ratio was determined by ^{31}P NMR.

Scheme 1. Large-Scale Preparation of 3c



1a 24 mmol 2g 20 mmol 3c

CuCl (5%) 20 min Yield: 94%

CuCl (0.5%) 20 h Yield: 90%

95% recovered

^{31}P NMR (162 MHz, $CDCl_3$): δ 28.0. HRMS-ESI calcd for $C_{19}H_{14}F_3O_2P(M + Na)^+$, 385.0581; found, 385.0579.

*Diphenyl(3-(trifluoromethyl)phenyl)phosphine Oxide (**3k**) (CAS no: 62754-67-0).* Colorless oil; 166 mg, 96% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 12.4 Hz, 1 H), 7.84–7.76 (m, 2 H), 7.67–7.62 (m, 4 H), 7.60–7.53 (m, 3 H), 7.49–7.44 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.4 (d, J = 10.3 Hz), 135.0, 134.0, 132.4 (d, J = 2.8 Hz), 132.1(d, 9.4 Hz), 131.7 (d, J = 105.5 Hz), 131.2 (d, J = 33.5, 12.0 Hz), 129.1 (d, J = 11.7 Hz), 128.9, 128.8, 123.7 (d, J = 273.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.9. MS-ESI: m/z 347.1, $[M + H]^+$.

*(3-Nitrophenyl)diphenylphosphine Oxide (**3l**) (CAS no: 31638-87-6).* Yellow oil; 132 mg, 82% yield. ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, 12.4 Hz, 1 H), 8.35 (d, J = 8.2 Hz, 1 H), 8.02 (t, J = 9.0 Hz, 1

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H), 7.67−7.62 (m, 5 H), 7.58−7.54 (m, 2 H), 7.49−7.45 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1 (d, J = 14.1 Hz), 137.7 (d, 9.5 Hz), 136.0 (d, J = 100.8 Hz), 132.6 (d, J = 2.8 Hz), 132.0 (d, J = 9.9 Hz), 131.1 (d, J = 106.0 Hz), 129.9 (d, J = 11.7 Hz), 128.9 (d, J = 12.6 Hz), 126.7 (d, J = 12.0 Hz), 126.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.3. MS-ESI: m/z 324.1, $[M + H]^+$.

*3-(Diphenylphosphoryl)benzoic Acid (**3m**) (CAS no: 2129-29-5).* White solid; 134 mg, 83% yield. ^{1}H NMR (400 MHz, DMSO): δ 8.22−8.19 (m, 2 H), 7.83−7.81 (m, 1 H), 7.63−7.60 (m, 7 H), 7.58−7.49 (m, 4 H). ^{13}C NMR (100 MHz, DMSO): δ 166.9, 136.1 (d, J = 11.2 Hz), 134.0 (d, J = 101.4 Hz), 133.1, 132.7 (d, J = 2.6 Hz), 132.5 (d, J = 10.6 Hz), 132.1, 132.0 (d, J = 10.0 Hz), 131.6 (d, J = 11.5 Hz), 129.8 (d, J = 11.7 Hz), 129.3 (d, J = 11.9 Hz). ^{31}P NMR (162 MHz, DMSO): δ 25.3. MS-ESI: m/z 323.1, $[M + H]^+$.

*Diphenyl(thiophen-2-yl)phosphine Oxide (**3n**) (CAS no: 56966-27-9).* Colorless oil; 115 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74−7.69 (m, 5 H), 7.55−7.51 (m, 2 H), 7.47−7.43 (m, 5 H), 7.18−7.16 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0 (d, J = 10.3 Hz), 134.1 (d, J = 112.0 Hz), 134.0 (d, J = 5.9 Hz), 133.0 (d, J = 110.5 Hz), 132.2 (d, J = 2.6 Hz), 131.8 (d, J = 10.5 Hz), 128.6 (d, J = 12.5 Hz),128.3 (d, J = 13.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.7. MS-ESI: m/z 285.1, $[M + H]^+$.

*Phenyl-di-p-tolylphosphine Oxide (**3o**) (CAS no: 18957-70-5).* White solid; 142 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.61 (m, 2 H), 7.55−7.49 (m, 4 H), 7.48−7.47 (m, 1 H), 7.43−7.39 (m, 2 H), 7.26−7.22 (m, 4 H), 2.37 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4 (d, J = 2.9 Hz), 133.1 (d, J = 104.1 Hz), 132.2 (d, J = 10.4 Hz), 132.1 (d, J = 10.1 Hz), 131.8 (d, J = 2.5 Hz), 129.5 (d, J = 106.5 Hz), 129.3 (d, J = 12.1 Hz), 128.5 (d, J = 12.2 Hz), 21.6. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 29.3. MS-ESI: m/z 329.1, $[M + Na]^+$.

*Bis(3-chlorophenyl)(phenyl)phosphine Oxide (**3p**) (CAS no: 54300-33-3).* Light yellow oil; 153 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.60 (m, 4 H), 7.58−7.56 (m, 1 H), 7.54−7.47 (m, 6 H), 7.43−7.39 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.3 (d, J = 16.3 Hz), 134.5 (d, J = 102.2 Hz), 132.6 (d, J = 2.7 Hz), 132.5 (d, J = 2.5 Hz), 132.0 (d, J = 28.5 Hz), 131.9 (d, J = 7.3 Hz), 131.1 (d, J = 106.0 Hz), 130.1 (d, J = 13.4 Hz), 130.0 (d, J = 9.5 Hz), 128.9 (d, J = 12.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.9. MS-ESI: m/z 347.1, $[M + H]^+$.

*Bis(4-fluorophenyl)(phenyl)phosphine Oxide (**3q**) (CAS no: 54300-32-2).* White solid; 128 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.62 (m, 6 H), 7.56−7.53 (m, 1 H), 7.47−7.45 (m, 2 H), 7.14 (t, J = 8.2 Hz, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2 (dd, J = 254.5, 3.8 Hz), 134.6 (dd, J = 11.9, 8.7 Hz), 132.3 (d, J = 2.0 Hz), 132.2 (d, J = 106.1 Hz), 132.0 (d, J = 10.4 Hz), 128.8 (d, J = 12.4 Hz), 128.5 (dd, J = 107.4, 4.0 Hz), 116.1 (dd, J = 21.1, 13.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.6. MS-ESI: m/z 315.1, $[M + H]^+$.

*Bis(4-methoxyphenyl)(phenyl)phosphine Oxide (**3r**) (CAS no: 799-55-3).* Light yellow oil; 162 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64−7.59 (m, 2 H), 7.57−7.50 (m, 4 H), 7.49−7.46 (m, 1 H), 7.42−7.38 (m, 2 H), 6.92 (dd, J = 8.9, 2.2 Hz, 4 H), 3.79 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.4 (d, J = 2.6 Hz), 134.0 (d, J = 11.2 Hz), 133.0, 132.0 (d, J = 10.1 Hz), 131.7 (d, J = 2.2 Hz), 128.4 (d, J = 12.8 Hz), 124.1 (d, J = 111.2 Hz), 114.1 (d, J = 13.1 Hz), 55.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.8. MS-ESI: m/z 339.2, $[M + H]^+$.

*Dimesityl(phenyl)phosphine Oxide (**3s**) (CAS no: 57368-26-0).* White solid; 145 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.41 (m, 4 H), 6.85−6.80 (m, 5 H), 2.26 (s, 6 H), 2.13 (m, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9 (d, J = 10.2 Hz), 141.0 (d, J = 2.7 Hz), 137.5 (d, J = 96.5 Hz), 132.4, 131.6 (d, J = 3.0 Hz), 131.2 (d, J = 11.3 Hz), 130.1 (d, J = 100.2 Hz), 128.7 (d, J = 12.4 Hz), 23.6 (d, J = 4.4 Hz), 21.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.2. MS-ESI: m/z 363.1, $[M + H]^+$.

*Bis(4-(dimethylamino)phenyl)(phenyl)phosphine Oxide (**3t**) (CAS no: 803-20-3).* White solid; 155 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65−7.61 (m, 2 H), 7.45−7.38 (m, 5 H), 7.35−7.32 (m, 2 H), 6.63−6.61 (m, 4 H), 2.91 (s, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1 (d, J = 2.0 Hz), 134.8 (d, J = 104.0 Hz), 133.3 (d, J = 11.0 Hz), 131.9 (d, J = 9.8 Hz), 130.9 (d, J = 2.6 Hz), 128.0 (d, J = 11.9 Hz), 118.0 (d, J = 115.5 Hz), 111.1 (d, J = 12.5 Hz), 39.8. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.7. MS-ESI: m/z 365.1, $[M + H]^+$.

*Bis(benzo[d][1,3]dioxol-5-yl)(phenyl)phosphine Oxide (**3u**).* Colorless oil; 172 mg, 94% yield. IR (film): 3427, 2901, 1479, 1422, 1242, 1036, 930, 704. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.44 (m, 4 H), 7.28−7.03 (m, 5 H), 6.87−6.85 (m, 2 H), 5.99 (s, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9 (d, J = 2.4 Hz), 148.0 (d, J = 18.2 Hz), 132.8 (d, J = 105.4 Hz), 132.0 (d, J = 10.3 Hz), 128.5 (d, J = 12.1 Hz), 127.6 (d, J = 11.0 Hz), 127.5 (d, J = 11.4 Hz), 125.8 (d, J = 108.5 Hz), 111.5 (d, J = 12.6 Hz), 108.7 (d, J = 15.0 Hz), 101.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.4. HRMS calcd for $C_{20}H_{15}O_5P(M + Na)^+$, 389.0554; found, 389.0555.

*Di([1,1′-biphenyl]-4-yl)(phenyl)phosphine Oxide (**3v**) (CAS no: 661451-80-5).* White solid; 163 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81−7.73 (m, 6 H), 7.71−7.69 (m, 4 H), 7.62−7.55 (m, 5 H), 7.52−7.44 (m, 6 H), 7.40−7.37 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8 (d, J = 2.8 Hz), 140.0, 133.3, 132.7 (d, J = 10.2 Hz), 132.2 (d, J = 10.2 Hz), 132.1 (d, J = 2.5 Hz), 131.2 (d, J = 106.1 Hz), 129.0, 128.7 (d, J = 12.6 Hz), 128.2, 127.3, 127.2. ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.9. MS-ESI: m/z 431.1, $[M + H]^+$.

*Ethyldiphenylphosphine Oxide (**3w**) (CAS no: 1733-57-9).* White solid; 108 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.63 (m, 4 H), 7.44−7.34(m, 6 H), 2.24−2.15 (m, 2 H), 1.11 (dt, J = 17.3, 7.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.8 (d, J = 98.5 Hz), 131.5 (d, J = 2.4 Hz), 130.7 (d, J = 8.9 Hz), 128.5 (d, J = 11.5 Hz), 22.7 (d, J = 73.9 Hz), 5.5 (d, J = 5.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.9. MS-ESI: m/z 231.1, $[M + H]^+$.

*Dipentyl(phenyl)phosphine Oxide (**3x**) (CAS no: 66232-90-4).* Light yellow oil; 93 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69−7.65 (m, 2 H), 7.52−7.44 (m, 3 H), 2.00−1.89 (m, 2 H), 1.87−1.77 (m, 2 H), 1.67−1.54 (m, 2 H), 1.46−1.21 (m, 10 H), 0.82 (t, J = 6.9 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.9 (d, J = 91.6 Hz), 131.5 (d, J = 2.5 Hz), 130.5 (d, J = 9.2 Hz), 128.7 (d, J = 11.0 Hz), 33.3 (d, J = 14.3 Hz), 30.0 (d, J = 68.0 Hz), 22.2, 21.2 (d, J = 3.8 Hz), 13.9. ^{31}P NMR (162 MHz, $CDCl_3$): δ 40.5. MS-ESI: m/z 267.1, $[M + H]^+$.

*Diphenyl(p-tolyl)phosphine Oxide (**3y**) (CAS no: 6840-28-4).* White solid; 66 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89−7.84 (m, 4 H), 7.78−7.70 (m, 4 H), 7.66−7.62 (m, 4 H), 7.48−7.45 (m, 2 H), 2.59 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.5 (d, J = 2.3 Hz), 133.4 (d, J = 104.1 Hz), 132.2 (d, J = 10.4 Hz), 132.1 (d, J = 10.0 Hz), 131.8 (d, J = 2.7 Hz), 129.3 (d, J = 12.3 Hz), 129.2 (d, J = 106.7 Hz), 128.5 (d, J = 11.9 Hz), 21.6. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 29.1. MS-ESI: m/z 293.2, $[M + H]^+$.

*Diphenyl(2,4,6-triisopropylphenyl)phosphine Oxide (**3z**).* White solid; mp 146−147 °C; 210 mg, 99% yield. IR (film): 3409, 3054, 2959, 1601, 1436, 1383, 1181, 1101, 701. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69−7.64 (m, 4 H), 7.46−7.41(m, 6 H), 7.09 (s, 2 H), 3.57−3.52 (m, 2 H), 2.92−2.86 (m, 1 H), 1.26 (d, J = 6.8 Hz, 6 H), 0.9 (d, J = 6.5 Hz, 12 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.1 (d, J = 10.7 Hz), 152.7, 137.3, 136.3, 131.7 (d, J = 10.0 Hz), 131.3, 128.5 (d, J = 12.2 Hz), 123.1 (d, J = 10.1 Hz), 34.2, 31.0 (d, J = 4.9 Hz), 24.5, 23.7. ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.1. HRMS-ESI calcd for $C_{27}H_{33}OP(M + Na)^+$, 427.2166; found, 427.2163.

*Dimethyl Mesitylphosphonate (**4a**) (CAS no: 68351-71-3).* Light yellow oil; 89 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (s, 2 H), 3.68 (d, J = 11.3 Hz, 6 H), 2.55 (s, 6 H), 2.25 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.0 (d, J = 12.5 Hz), 142.1 (d, J = 2.4 Hz), 130.4 (d, J = 15.6 Hz), 121.0 (d, J = 182.4 Hz), 51.7 (d, J = 5.7 Hz), 23.0 (d, J = 2.3 Hz), 21.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.5. MS-ESI: m/z 229.1, $[M + H]^+$.

*Diethyl Phenylphosphonate (**4b**) (CAS no: 1754-49-0).* Colorless oil; 96 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79−7.74 (m, 2 H), 7.52−7.48 (m, 1 H), 7.44−7.39 (m, 2 H), 4.15−3.98 (m, 4 H), 1.27 (t, J = 6.9 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.4 (d, J = 2.9 Hz), 131.8 (d, J = 9.8 Hz), 128.6 (d, J = 188.3 Hz), 128.5 (d, J = 14.9 Hz), 62.1 (d, J = 5.3 Hz), 16.3 (d, J = 6.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 18.7. MS-ESI: m/z 215.1, $[M + H]^+$.

*Diethyl (4-Bromophenyl)phosphonate (**4c**) (CAS no: 20677-12-7).* Colorless oil; 134 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ

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7.64−7.59 (m, 2 H), 7.58−7.52 (m, 2 H), 4.09−4.01 (m, 4 H), 1.30−1.22 (m, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.3 (d, J = 10.9 Hz), 131.9 (d, J = 15.5 Hz), 127.6 (d, J = 190.8 Hz), 127.5 (d, J = 4.4 Hz), 62.3 (d, J = 5.5 Hz), 16.3 (d, J = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.67. MS-ESI: m/z 293.1, $[M + H]^+$.

*Diethyl (3-(Trifluoromethyl)phenyl)phosphonate (**4d**) (CAS no: 77918-46-8).* Light yellow oil; 126 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 13.4 Hz, 1 H), 8.00−7.95 (m, 1 H), 7.79−7.77 (m, 1 H), 7.59−7.58 (m, 1 H), 4.21−4.06 (m, 4 H), 1.31 (t, J = 7.1 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.1 (d, J = 9.2 Hz), 131.1 (dd, J = 15.2, 32.2), 130.5 (d, J = 190.3, Hz), 129.3 (d, J = 13.6 Hz), 129.0 (d, J = 3.7 Hz), 128.6 (d, J = 10.5 Hz), 123.8 (dd, J = 274.0, 11.0 Hz), 62.6 (d, J = 5.3), 16.4 (d, J = 6.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.2. MS-ESI: m/z 283.1, $[M + H]^+$.

*Diethyl (4-Methoxyphenyl)phosphonate (**4e**) (CAS no: 3762-33-2).* Light yellow oil; 116 mg, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.72−7.67 (m, 2 H), 6.92−6.90 (m, 2 H), 4.09−3.97 (m, 4 H), 3.79 (s, 3 H), 1.26 (t, J = 7.1 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, J = 3.8 Hz), 133.8 (d, J = 11.2 Hz), 119.6 (d, J = 194.6 Hz), 114.0 (d, J = 16.2 Hz), 61.9 (d, J = 5.1 Hz), 55.4, 16.3 (d, J = 6.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.6. MS-ESI: m/z 245.1, $[M + H]^+$.

*Dibenzyl Phenylphosphonate (**4f**) (CAS no: 19236-61-4).* Light yellow oil; 144 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.88−7.83 (m, 2 H), 7.58−7.46 (m, 4 H), 7.40−7.26 (m, 9 H), 5.16−5.05 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.2 (d, J = 6.8 Hz), 132.6 (d, J = 2.9 Hz), 131.9 (d, J = 9.8 Hz), 128.6, 128.5, 128.4, 128.3 (d, J = 63.6 Hz), 128.0 (d, J = 189.8 Hz), 67.6 (d, J = 5.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.70. MS-ESI: m/z 339.1, $[M + H]^+$.

*Diallyl Phenylphosphonate (**4g**) (CAS no: 2948-89-2).* Colorless oil; 111 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.75 (dd, J = 13.6, 7.2 Hz, 2 H), 7.49−7.46 (m, 1 H), 7.41−7.36 (m, 2 H), 5.90−5.81 (m, 2 H), 5.21 (d, J = 53.9 Hz, 2 H), 5.18 (d, J = 46.7 Hz, 2 H), 4.56 − 4.42 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.7 (d, J = 7.0 Hz), 132.5 (d, J = 2.8 Hz), 131.7 (d, J = 10.3 Hz), 128.4 (d, J = 15.4 Hz), 127.7 (d, J = 189.0 Hz), 117.9, 66.4 (d, J = 5.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.5. MS-ESI: m/z 239.1, $[M + H]^+$.

*Ethyl Diphenylphosphinate (**4h**) (CAS no: 1733-55-7).* Light yellow oil;116 mg, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ7.79−7.74 (m, 4 H), 7.45−7.42 (m, 2 H), 7.39−7.35 (m, 4 H), 4.08−4.01 (m, 2 H), 1.30 (t, J = 6.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.0 (d, J = 2.5 Hz), 131.5 (d, J = 10.4 Hz), 131.2 (d, J = 137.0 Hz), 128.5 (d, J = 13.1 Hz), 61.0 (d, J = 5.9 Hz), 16.4 (d, J = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.2. MS-ESI: m/z 247.1, $[M + H]^+$.

*(4-Nitrophenyl)diphenylphosphine Oxide (**4i**) (CAS no: 5032-71-3).* Yellow solid; 113 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 8.2 Hz, 2 H), 7.85 (t, J = 9.5 Hz, 2 H), 7.65−7.60 (m, 4 H), 7.57−7.54 (m, 2 H), 7.48−7.46 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 140.5 (d, J = 98.6 Hz), 133.3 (d, J = 10.7 Hz), 132.6 (d, J = 2.4 Hz), 132.0 (d, J = 10.1 Hz), 131.1 (d, J = 106.0 Hz), 128.9 (d, J = 12.5 Hz), 123.4 (d, J = 12.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.4. MS-ESI: m/z 324.1, $[M + H]^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

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Notes

The authors declare no competing financial interest.

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