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Copper-Catalyzed Coupling Reaction of Arylhydrazines and Trialkylphosphites

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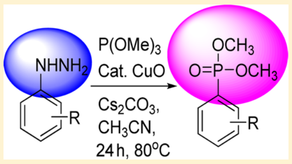
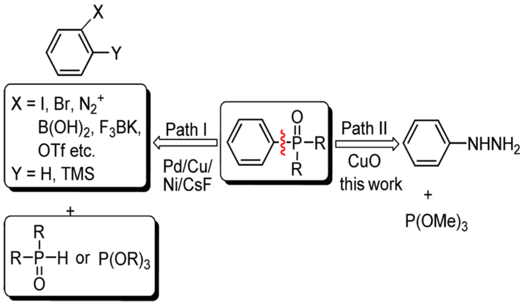
Supporting Information

ABSTRACT: A novel CuO-catalyzed coupling reaction of arylhydrazines with trialkyl phosphites to afford arylphosphonates is described. The reaction proceeded at 80 °C in air without external reductants, oxidants, and ligands.



Carbon–phosphorus bond formation is a current topic in organic chemistry.[1] The Michaelis–Arbuzov reaction is a well-known method for C–P bond formation; however, it is not applicable to the formation of aryl C–P bonds.[2] Therefore, during the past 3 decades, great efforts have been focused on the metal-catalyzed cross-coupling reactions of functionalized arenes with phosphorus reagents. Until now, aryl halides,[3] triflates,[4a] imidazolylsulfonates,[4b] diazonium salts,[4c] arylboronic acids or aryltrifluoroborates,[4d,e] and *o*-aryl silyl triflates[4f] have been used for the reaction catalyzed/promoted by Pd, Cu, Ni, and CsF reagents to construct C(sp^2)–P bonds (Scheme 1, path I). As part of our research on the C–P bond formation catalyzed/promoted by copper or manganese reagents,[5] this note reports the first example of a coupling reaction of phenylhydrazine with trimethylphosphite catalyzed by CuO (Scheme 1, path II).

Scheme 1



When the model reaction of phenylhydrazine (**1a**) with trimethylphosphite (**2a**) was performed in refluxing CH_3CN in the presence only of inorganic base Cs_2CO_3, no reaction took place. After addition of 10 mol % CuO and 1,10-phenanthrolin (**L1**) as ligand, the reaction proceeded smoothly to afford the desired product dimethyl phenylphosphonate (**3a**) in 46% yield (Table 1, entry 2). Followed by screening different ligands such as proline (**L2**), 2,2′-bipyridine (**L3**), 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (**L4**), *N*,*N*′-dimethylethylenediamine (**L5**), PPh_3 (**L6**), and 2,2′-biimidazole (**L7**) (Figure 1 and Table 1, entries 4–9), the results showed that **L7** works well for the reaction (Table 1, entry 9). Occasionally, we found that the reaction could also work in the absence of any ligand; however, in the presence of $Cu(OAc)_2$, the yield was reduced to 57% (Table 1, entry 10). Interestingly, in the case of CuO/ligand-free conditions, the reaction gave **3a** in 71% yield (Table 1, entry 11), which is higher than the yields of products synthesized in the presence of ligands **L1**, **L6**, and **L7** (Table 1, entries 3, 8, and 9). Among the different inorganic and organic bases employed for the reaction, Cs_2CO_3 was the best (Table 1, entries 11–15). Polar solvents such as CH_3CN, DMSO, DMF, and 1,4-dioxane and a representative nonpolar solvent, toluene, were explored, and CH_3CN led to the highest yield (Table 1, entries 11 and 16–19). The catalytic activity of Cu(I) and Cu(II) salts such as CuI, CuCl, CuBr, $CuCl_2$, and $Cu(OAc)_2$ were investigated; they all catalyzed this reaction in air, and CuO gave the best yield (Table 1, entries 11 and 20–23). Other than the above-mentioned factors, the effects of catalyst loading and reaction temperature and time were also investigated, and the optimal reaction conditions were determined to be 10 mol % CuO as catalyst and Cs_2CO_3 as base in CH_3CN at 80 °C for 24 h in air (Table 1, entries 24–30).

With the promising results obtained in the model reaction, we then examined the substrate scope of arylhydrazines under the optimized reaction conditions (10 mol % CuO as catalyst and Cs_2CO_3 as base in CH_3CN at 80 °C for 24 h in air). As seen in Table 2, electron-donating substituents such as alkyl

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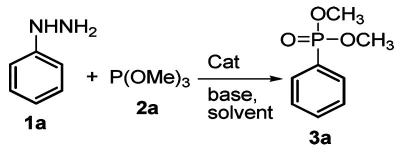
Table 1. Optimization of the Reaction Conditions[a]



entry	catalyst	solvent	base	ligand	yield[b] (%)
1		CH_3CN	Cs_2CO_3		N.D.[c]
2	CuO	CH_3CN	Cs_2CO_3	**L1**	46
3	$Cu(OAc)_2$	CH_3CN	Cs_2CO_3	**L1**	62
4	CuO	CH_3CN	Cs_2CO_3	**L2**	35
5	CuO	CH_3CN	Cs_2CO_3	**L3**	43
6	CuO	CH_3CN	Cs_2CO_3	**L4**	24
7	CuO	CH_3CN	Cs_2CO_3	**L5**	46
8	CuO	CH_3CN	Cs_2CO_3	**L6**	62
9	CuO	CH_3CN	Cs_2CO_3	**L7**	69
10	$Cu(OAc)_2$	CH_3CN	Cs_2CO_3		57
11	CuO	CH_3CN	Cs_2CO_3		71
12	CuO	CH_3CN			42
13	CuO	CH_3CN	K_2CO_3		trace
14	CuO	CH_3CN	$N(Et)_3$		57
15	CuO	CH_3CN	KOH		trace
16	CuO	DMSO	Cs_2CO_3		<10
17	CuO	DMF	Cs_2CO_3		<10
18	CuO	11,4-dioxane	Cs_2CO_3		62
19	CuO	toluene	Cs_2CO_3		21
20	CuI	CH_3CN	Cs_2CO_3		55
21	CuBr	CH_3CN	Cs_2CO_3		47
22	CuCl	CH_3CN	Cs_2CO_3		51
23	$CuCl_2$	CH_3CN	Cs_2CO_3		59
24[d]	CuO	CH_3CN	Cs_2CO_3		28
25[e]	CuO	CH_3CN	Cs_2CO_3		62
26[f]	CuO	CH_3CN	Cs_2CO_3		67
27[g]	CuO	CH_3CN	Cs_2CO_3		39
28[h]	CuO	CH_3CN	Cs_2CO_3		60
29[i]	CuO	CH_3CN	Cs_2CO_3		68
30[j]	CuO	CH_3CN	Cs_2CO_3		71

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), base (3.0 mmol), **L** (10 mol %), and catalyst (10 mol %) in CH_3CN (3.0 mL) at 80 °C for 24 h in air. [b] Isolated yields. [c] N.D., not detected. [d] Using 1 mol % CuO. [e] Using 5 mol % CuO. [f] Using 20 mol % CuO. [g] At 25 °C. [h] At 60 °C. [i] At 100 °C. [j] For 36 h.

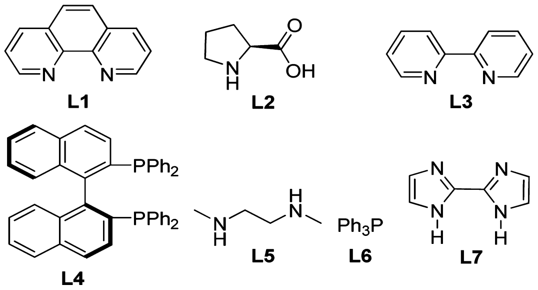


Figure 1. Structure of the ligands.

and methoxy groups on the aryl ring of arylhydrazines (**1**) facilitated the reaction to afford the arylphosphonates (**3**) in moderate to good yields (Table 2, entries 3–7). On the contrary, electron-withdrawing groups such as F, Cl, Br, $COOCH_3$, CN, and NO_2 were unfavorable for the reaction and led to lower yields (Table 2, entries 8–16). The role of the ortho substituents for the reaction was then probed. As shown in Table 2, arylhydrazines (**1**) with ortho substituents such as methyl, ethyl, Cl, and NO_2 groups all suppressed the reaction (Table 2, entries 2, 14, 16, 17, 18, and 19). With more bulky ortho substituents, the yield became lower (Table 2, entries 2, 17, and 19), and when NO_2 or two ethyl groups occupied one or two ortho positions, the reaction was hindered (Table 2, entries 16 and 18). Triethylphosphite and triphenylphosphite were also applied to the reaction with 4-methoxyphenylhydrazine, and the results indicated that the former gave the expected product in 68% yield, whereas the latter afforded a trace product (Table 2, entries 20 and 21).

The plausible mechanism for the CuO-catalyzed coupling reaction of arylhydrazines and trimethylphosphite is proposed in Scheme 2. Cu(II) species are first reduced to Cu(I) by trimethylphosphite (**2**) in situ; then, the aryl radical (**4**) generated from arylhydrazines (**1**) oxidized by air (O_2)[6] and trimethylphosphite (**2**) combine with Cu(I) species to form a Cu(III) complex (**5**). The arylphosphonates (**3**) are produced through the formation of a Cu(III) complex (**6**) via a CH_3 radical leaving followed by a ligand-coupling reaction.

We extended this method to use different substituents on the hydrazines such as sulfonyl, acyl, and alkyl hydrazines; regretfully, the expected results were not obtained (Table 3, entries 1–3).

In conclusion, a novel method for carbon–phosphorus bond formation was developed through the coupling reaction of arylhydrazines with trialkylphosphites catalyzed by 10 mol % CuO. The reaction proceeded under mild conditions in air without external reductants, oxidants, and ligands. Commercially available Cu(II) and Cu(I) salts could all catalyze this reaction, but the real catalytic species should be Cu(I). This methodology provides an effective and cheap way to the synthesis of arylphosphonates.

EXPERIMENTAL SECTION

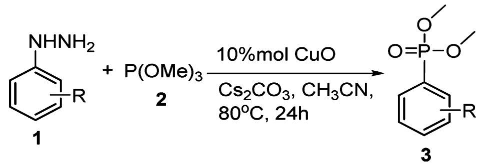
General Information. ^1H and ^{13}CNMR spectra were recorded in $CDCl_3$ (internal standard at 7.26 ppm for ^1H and 77.5 ppm for ^{13}C) using a 300 or 400 MHz spectrometer. HRMS data were recorded on a TOF instrument using the ESI technique. Column chromatography was performed with 300–400 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted.

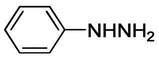
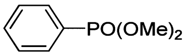
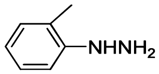
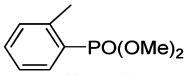
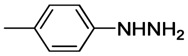
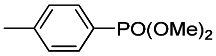
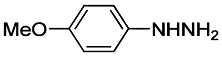
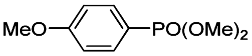
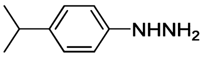
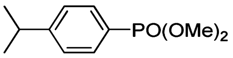
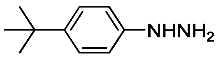
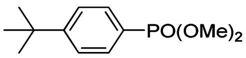
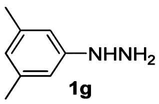
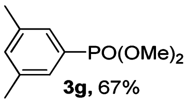
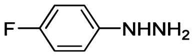
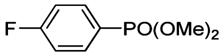
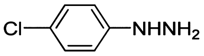
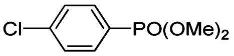
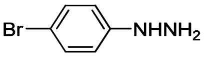
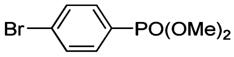
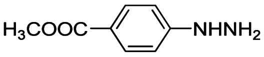
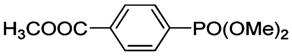
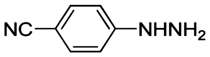
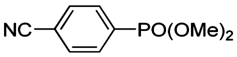
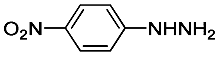
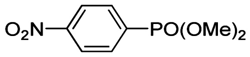
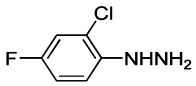
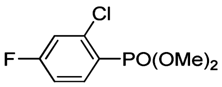
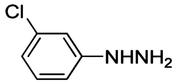
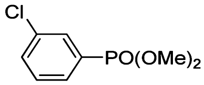
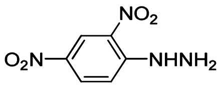
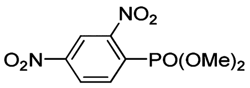
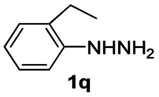
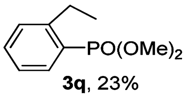
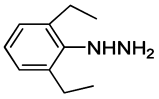
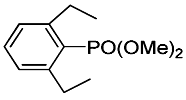
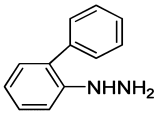
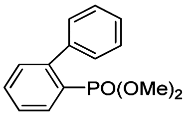
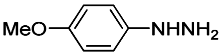
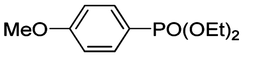
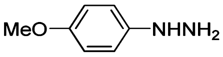
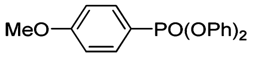
General Procedure for the Preparation of Compound 3. Arylhydrazine or its salt (1 mmol), trimethylphosphite (248 mg, 2 mmol), and Cs_2CO_3 (978 mg, 3 mmol) were added to a flask with CH_3CN (3 mL), the mixture was stirred for 15 min at room temperature in air, and CuO (8.0 mg, 0.1 mmol) was then added. After the reaction mixture was stirred at 80 °C for 24 h in air, it was allowed to cool to room temperature, diluted with diethyl ether (5 mL), and filtered, and the filtrate was concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate 4:1 to 2:1) to afford desired pure product **3**.

Dimethyl Phenylphosphonate (3a). Yellow oil (133.0 mg, 71% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.90–7.70 (m, 2H), 7.67–7.52 (m, 1H), 7.51–7.40 (m, 2H), 3.77 (d, J = 11.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.1, 132.2 (d, J = 9.8 Hz), 129.0 (d, J = 14.9 Hz), 127.3 (d, J = 180.4 Hz), 53.0 (d, J = 5.4 Hz). MS (ESI-TOF) m/z: (M + 1)$^+$ calcd for $C_8H_{12}O_3P$, 187; found, 187.[7]

Dimethyl *o*-Tolylphosphonate (3b). Yellow oil (129.3 mg, 58% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ 7.89 (dd, J = 6.0, 10.8 Hz, 1H), 7.50–7.40 (m, 1H), 7.30–7.10 (m, 2H), 3.76 (d, J = 8.4 Hz, 6H), 2.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.3 (d, J = 10.0 Hz), 134.4 (d, J = 10.0 Hz), 133.1 (d, J = 3.0 Hz), 131.6 (d, J = 15.0 Hz), 126.1 (d, J = 185.0 Hz), 125.8 (d, J = 15.0 Hz), 52.8 (d, J = 6.0 Hz), 21.5 (d, J = 4.0 Hz). HRMS (ESI-TOF) m/z: (M + Na)$^+$ calcd for $C_9H_{13}NaO_3P$, 223.0495; found, 223.0491.

Table 2. CuO-Catalyzed Coupling Reaction of Arylhydrazines and Trimethylphosphite[a]



entry	hydrazine **1**	product **3** and yield[b]
1	 **1a**	 **3a, 71%**
2	 **1b**	 **3b, 58%**
3	 **1c**	 **3c, 70%**
4	 **1d**	 **3d** 78%[c]
5	 **1e**	 **3e** 73%
6	 **1f**	 **3f** 72%
7	 **1g**	 **3g, 67%**
8	 **1h**	 **3h** 42%
9	 **1i**	 **3i** 46%
10	 **1j**	 **3j** 41%
11	 **1k**	 **3k** 46%
12	 **1l**	 **3l** trace[d]
13	 **1m**	 **3m** 38%
14	 **1n**	 **3n** trace[d]
15	 **1o**	 **3o, 36%**
16	 **1p**	 **3p**, trace[d]
17	 **1q**	 **3q**, 23%
18	 **1r**	 **3r, N.D.**[e]
19	 **1s**	 **3s, trace**[d]
20	 **1d**	 **3t** 68%
21	 **1d**	 **3u** trace[d]

[a] Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), Cs_2CO_3 (3.0 mmol), and CuO (10 mol %) in CH_3CN (3.0 mL) at 80 °C for 24 h in air. [b] Isolated yield. [c] 4-Methoxyphenylhydrazine (1.0 and 8.0 mmol) afforded product **3d** in 78 and 71% yield, respectively. [d] Detected by LC−MS. [e] N.D., not detected.

Dimethyl *p*-Tolylphosphonate (3c). Yellow oil (140.0 mg, 70% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.69 (dd, J = 6.0, 9.9 Hz, 2H), 7.35−7.20 (m, 2H), 3.74 (d, J = 11.2 Hz, 6H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7, 132.3(d, J = 10.2 Hz), 129.7 (d, J = 15.4 Hz), 123.9 (d, J = 142.4 Hz), 52.9 (d, J = 5.2 Hz), 22.0. MS (ESI-TOF) *m*/*z*: $(M + 1)^+$ calcd for $C_9H_{14}O_3P$, 201; found, 201.[7]

Dimethyl (4-Methoxyphenyl)phosphonate (3d). Yellow oil (168.2 mg, 78% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74 (dd, J = 8.7, 12.9 Hz, 2H), 6.98 (dd, J = 3.3, 8.7 Hz, 2H), 3.86 (s, 3H), 3.74 (d, J = 11.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.6, 134.3 (d, J = 8.5 Hz), 118.5 (d, J = 146.2 Hz), 114.6 (d, J = 10.5 Hz), 55.7, 52.9 (d, J = 3.8 Hz). MS (ESI-TOF) *m*/*z*: $(M + 1)^+$ calcd for $C_9H_{14}O_4P$, 217; found, 217.[7]

Dimethyl (4-Isopropylphenyl)phosphonate (3e). Yellow oil (167.2 mg, 73% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (dd, J = 8.0, 13.2 Hz, 2H), 7.50−7.30 (m, 2H), 3.75 (d, J = 10.8 Hz, 6H), 3.00−2.90 (m, 1H), 1.26 (d, J = 2.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.3, 132.3 (d, J = 7.9 Hz), 127.1 (d, J = 15.4 Hz), 124.5 (d, J = 182.2 Hz), 52.9 (d, J = 8.3 Hz), 34.6, 23.9. HRMS (MALDI-TOF) *m*/*z*: $(M + 1)^+$ calcd for $C_{11}H_{18}O_3P$, 229.0995; found, 229.0988.

Dimethyl (4-*tert*-Butylphenyl)phosphonate (3f). Yellow oil (175.0 mg, 72% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (dd, J = 8.4, 13.2 Hz, 2H), 7.53−7.40 (m, 2H), 3.75 (d, J = 11.2 Hz, 6H), 1.33 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5, 132.0 (d, J = 10.2 Hz), 125.8 (d, J = 15.0 Hz), 123.4 (d, J = 189.9 Hz), 52.8 (d, J = 5.2 Hz),

Scheme 2. Plausible Catalytic Mechanism

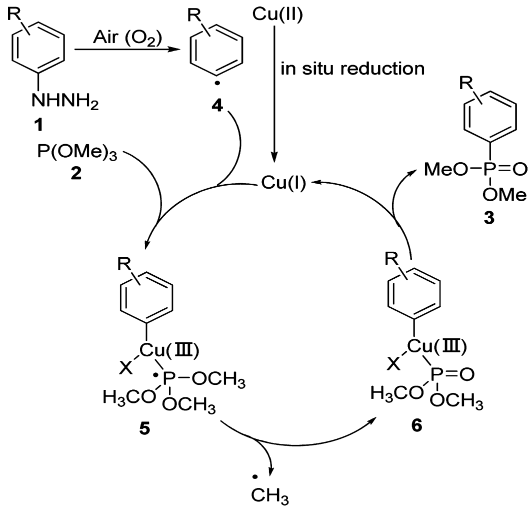
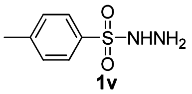
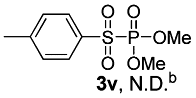
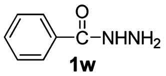
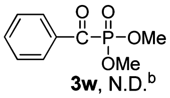
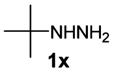
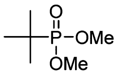


Table 3. CuO-Catalyzed Coupling Reaction of Sulfonyl, Acyl, and Alkyl Hydrazines with Trimethylphosphite[a]

$$\underset{\mathbf{1}}{\text{R–NHNH}_2} + \underset{\mathbf{2}}{\text{P(OMe)}_3} \xrightarrow[\text{Cs}_2\text{CO}_3,\ \text{CH}_3\text{CN},\ 80\ ^\circ\text{C},\ 24\ \text{h}]{10\%\text{mol CuO}} \underset{\mathbf{3}}{\text{Product}}$$

entry	hydrazine **1**	product **3** and yield
1	 **1v**	 **3v**, N.D.[b]
2	 **1w**	 **3w**, N.D.[b]
3	 **1x**	 **3x**, N.D.[b]

[a]Reaction conditions: **1** (1.0 mmol), **2** (2.0 mmol), Cs_2CO_3(3.0 mmol), and CuO (10 mol %) in CH_3CN (3.0 mL) at 80 °C for 24 h in air. [b]N.D., not detected.

35.3, 31.3. HRMS (ESI-TOF) m/z: $(M + 1)^+$ calcd for $C_{12}H_{20}O_3P$, 243.1145; found, 243.1144.

Dimethyl (3,5-Dimethylphenyl)phosphonate (3g). Yellow oil (158.2 mg, 67% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (d, J = 13.3 Hz, 2H), 7.19 (s, 1H), 3.75 (d, J = 11.2 Hz, 6H), 2.35 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.6 (d, J = 13.5 Hz), 134.7 (d, J = 2.3 Hz), 129.7 (d, J = 9.7 Hz), 126.6 (d, J = 185.8 Hz), 52.9 (d, J = 5.3 Hz), 21.4. HRMS (ESI-TOF) m/z: $(M + Na)^+$ calcd for $C_{10}H_{15}NaO_3P$, 237.0651; found, 237.0652.

Dimethyl (4-Fluorophenyl)phosphonate (3h). Yellow oil (86.1 mg, 42% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90−7.70 (m, 2H), 7.21−7.10 (m, 2H), 3.77 (dd, J = 2.0, 11.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.6 (dd, J = 4.9, 251.4 Hz), 134.9 (dd, J = 9.1, 11.1 Hz), 123.6 (dd, J = 3.5, 193.2 Hz), 116.3 (dd, J = 16.3, 21.3 Hz), 53.1 (d, J = 7.3 Hz). MS (ESI-TOF) m/z: $(M + 1)^+$ calcd for $C_8H_{11}FO_3P$, 205; found, 205 .[7]

Dimethyl(4-Chlorophenyl)phosphonate (3i). Yellow oil (101.2 mg, 46% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71−7.60 (m, 2H), 7.45−7.30 (m, 2H), 3.68 (d, J = 10.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.6 (d, J = 6.4 Hz), 133.6 (d, J = 14.2 Hz), 129.2 (d, J = 3.9 Hz), 126.2 (d, J = 190.7 Hz), 53.0 (d, J = 5.5 Hz). HRMS (ESI-TOF) m/z: $(M + 1)^+$ calcd for $C_8H_{11}ClO_3P$, 221.0129; found, 221.0129.

Dimethyl (4-Bromophenyl)phosphonate (3j). Yellow oil (108.2 mg, 41% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90−7.70 (m, 2H), 7.60−7.40 (m, 2H), 3.77 (d, J = 5.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.2, 132.3 (d, J = 9.8 Hz), 129.0 (d, J = 15.6 Hz), 127.4 (d, J = 187.6 Hz), 53.2 (d, J = 5.3 Hz). HRMS (ESI-TOF) m/z: $(M + 1)^+$ calcd for $C_8H_{11}BrO_3P$, 264.9629; found, 264.9632.

Dimethyl (4-Methoxycarbonyl)phosphonate (3k). Yellow oil (112.3 mg, 46% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.14 (dd, J = 10.0, 4.0 Hz, 2H), 7.89 (dd, J = 12.8, 8.40 Hz, 2H), 3.95 (s, 3H), 3.79 (d, J = 11.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2, 133.8 (d, J = 2.4 Hz), 131.9 (d, J = 7.5 Hz), 131.8 (d, J = 139.7 Hz), 129.5 (d, J = 11.3 Hz), 52.9 (d, J = 4.2 Hz), 52.5. HRMS (ESI-TOF) m/z: $(M + 1)^+$ calcd for $C_{10}H_{14}O_5P$, 245.0579; found, 245.0579.

Dimethyl (4-Nitrophenyl)phosphonate (3m). Yellow oil (88.1 mg, 38% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65−7.50 (m, 2H), 6.80−6.60 (m, 2H), 3.71 (d, J = 13.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.1, 132.3 (d, J = 9.7 Hz), 129.0 (d, J = 14.9 Hz), 127.3 (d, J = 187.9 Hz), 53.0 (d, J = 5.5 Hz). HRMS (ESI-TOF) m/z: $(M + 1)^+$ calcd for $C_8H_{11}NO_5P$, 232.0369; found, 232.0374.

Dimethyl (3-Chlorophenyl)phosphonate (3o). Yellow oil (79.5 mg, 36% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.15 (t, J = 8.0 Hz, 1H), 6.90−6.80 (m, 1H), 6.70 (d, J = 1.6 Hz, 1H), 6.59 (d, J = 8.0 Hz, 1H), 3.73 (s, 3H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.7 (d, J = 154.6 Hz), 130.9, 125.4, 121.3, 113.2, 111.5, 53.9. HRMS (ESI-TOF) m/z: $(M + 1)^+$ calcd for $C_8H_{11}ClO_3P$, 221.0129; found, 221.0127.

Dimethyl (2-Ethylphenyl)phosphonate (3q). Yellow oil (49.2 mg, 23% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (dd, J = 16.0, 7.6 Hz, 1H), 7.49 (dd, J = 8.0, 7.2 Hz, 1H), 7.34 (dd, J = 8.0, 6.6 Hz, 1H), 7.30−7.20 (m, 1H), 3.77 (d, J = 10.8 Hz, 6H), 2.96 (q, J = 7.6, 2H), 1.26 (t, J = 7.6, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.4 (d, J = 8.4 Hz), 134.0 (d, J = 7.6 Hz), 132.8 (d, J = 2.2 Hz), 129.6 (d, J = 11.3 Hz), 125.4 (d, J = 11.1 Hz), 125.0 (d, J = 137.8 Hz), 52.5 (d, J = 4.3 Hz), 27.2 (d, J = 2.8 Hz), 15.6. HRMS (ESI-TOF) m/z: $(M + 1)^+$ calcd for $C_{10}H_{16}O_3P$, 215.0837; found, 215.0837.

Diethyl (4-Methoxyphenyl)phosphonate (3t). Yellow oil (165.9 mg, 68% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76 (dd, J = 12.0, 8.8 Hz, 2H), 7.10−6.89 (m, 2H), 4.26−3.96 (m, 2H, CH_2), 3.85 (s, 3H, CH_3), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.2 (d, J = 2.6 Hz), 134.1 (d, J = 8.5 Hz), 119.8 (d, J = 145.1 Hz), 114.4 (d, J = 11.9 Hz), 62.3 (d, J = 3.8 Hz), 55.7 (d, J = 2.0 Hz), 16.7 (d, J = 4.9 Hz). MS (ESI-TOF) m/z: $(M + 1)^+$ calcd for $C_{11}H_{18}O_4P$, 245; found, 245.[8]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of all of the products. 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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