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# A Versatile and Efficient Ligand for Copper-Catalyzed Formation of C–N, C–O, and P–C Bonds: Pyrrolidine-2-Phosphonic Acid Phenyl Monoester

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**Abstract:** A new and readily available bidentate ligand, namely, pyrrolidine-2-phosphonic acid phenyl monoester (PPAPM), has been developed for the copper-catalyzed formation of C–N, C–O, and P–C bonds, and various N-, O-, and P-arylation products were synthesized in good to excellent yields by using the CuI/PPAPM catalyst system. Addition of the PPAPM ligand greatly increases the reactivity of the copper catalyst, and the resulting versatile and efficient catalyst system is of widespread and practical application in cross-coupling reactions.

**Keywords:** arylation · copper · cross-coupling · homogeneous catalysis · N,O ligands

## Introduction

Transition-metal-catalyzed formation of C–N,[1] C–O,[2] and P–C[3] bonds by cross-coupling reactions is a powerful means for the preparation of numerous important products in biological, pharmaceutical, and materials sciences. Although some significant achievements in the palladium-catalyzed N-arylation of amines/amides,[4] O-arylation of substituted phenols,[5] and formation of P–C bonds[6] have been made, the drawbacks of the catalyst systems, such as sensitivity to air, high cost, and toxicity, limit their applications. During the past few years, great progress in copper-catalyzed N-arylation of amines/amides[7] and O-arylation of substituted phenols[8] and alcohols[9] has been made, which strongly relied on the utilization of some special bidentate additives, for example, aliphatic diamines,[10] 1,10-phenanthroline and its derivatives,[11] ethylene glycol,[12a] diethylsalicylamide,[12b] amino acids,[13] oxime-type and Schiff-base ligands,[14] thiophene-2-carboxylate,[15] bidentate phosphines,[16] and diphosphinidenecyclobutene[17] for N-arylation of amines/amides; 1-naphthoic acid,[8a] 2,2,6,6-tetramethylheptane-3,5-dione,[8b] phosphazene $P_4$-*t*Bu base,[8c] *N*,*N*-dimethylglycine,[8d] 8-hydroxyquinoline,[8e] neocuproine,[8f] salicylaldoxime (Salox)[8g] for O-arylation of substituted phenols and alcohols. However, to the best of our knowledge, most of the above-mentioned ligands can only be used in one or two kinds of copper-catalyzed reactions, examples of copper-mediated P–C bond formation are rare,[18] and there is no general ligand for copper-catalyzed carbon–heteroatom (N, O, P) bond formation in cross-coupling reactions. Hence, the search for new and general ligands is essential for copper-catalyzed cross-coupling reactions. Here we report on pyrrolidine-2-phosphonic acid phenyl monoester (PPAPM) as a versatile and efficient bidentate ligand for the copper-catalyzed formation of C–N, C–O, and P–C bonds.

## Results and Discussion

The ligand PPAPM was readily synthesized according to the reported procedure. Reaction of 1-pyrroline trimer with diphenyl phosphite led to diphenyl pyrrolidine-2-phosphonate, whose hydrolysis in LiOH provided PPAPM (Scheme 1).[19]

**Copper-catalyzed N-arylation reactions**: We first chose aniline and bromobenzene as model substrates to optimize the catalysis conditions (copper source, base, solvent, amount of catalyst and PPAPM ligand) to achieve the best results in the cross-coupling reactions (Table 1). $CuSO_4$, CuBr, $CuCl_2$, CuI (entries 1–4 in Table 1) were tested as copper source in

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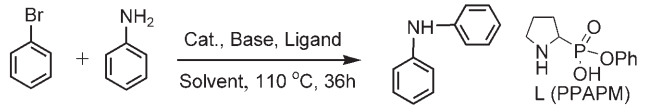
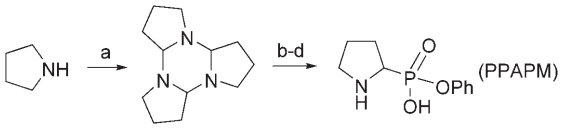
Table 1. Copper-catalyzed N-arylation of aniline: optimization of the catalysis conditions and comparison of PPAPM with standard ligands.[a]




| Entry | Catalyst | Base | Solvent | Yield [%][b] |
|---|---|---|---|---|
| 1 | $CuSO_4$ | $K_2CO_3$ | toluene | 39 |
| 2 | CuBr | $K_2CO_3$ | toluene | 46 |
| 3 | $CuCl_2$ | $K_2CO_3$ | toluene | 35 |
| 4 | CuI | $K_2CO_3$ | toluene | 57 |
| 5 | CuI | $Na_2CO_3$ | toluene | 30 |
| 6 | CuI | $Cs_2CO_3$ | toluene | 51 |
| 7 | CuI | $K_3PO_4$ | toluene | 65 |
| 8 | CuI | $K_3PO_4$ | 1,4-dioxane | 53 |
| 9 | CuI | $K_3PO_4$ | DMF | 70 |
| 10 | CuI | $K_3PO_4$ | DMF | trace[c] |
| 11 | CuI | $K_3PO_4$ | DMF | 57[d] |
| 12 | CuI | $K_3PO_4$ | DMF | 59[e] |

[a] Reaction conditions: bromobenzene (1.5 mmol), aniline (1.0 mmol), catalyst (0.05 mmol), ligand (0.2 mmol), base (2.0 mmol), solvent (2.0 mL) under $N_2$. [b] Yield of isolated product. [c] No addition of PPAPM. [d, e] With proline and *N,N,N′,N′*-tetramethylethyldiamine, respectively, as standard ligand instead of PPAPM for the coupling reaction under our optimal conditions.




Scheme 1. Synthesis of PPAPM. a) 3 equiv NaOH, 25% aqueous $Na_2S_2O_8$, 0.0005 equiv $AgNO_3$, 0°C to RT; b) 3 equiv $HP(O)(OPh)_2$, 85°C, $N_2$; c) anhydrous $Et_2O$, gaseous HCl; d) $CH_3CN$, LiOH (1 M aqueous).

the Ullmann condensation with toluene as solvent and $K_2CO_3$ as base, and the results showed that CuI was the best catalyst. In the following optimization process, we found that coupling reactions with $K_3PO_4$ as base (entries 4–7 in Table 1) and DMF as the solvent (entries 7–9 in Table 1) could afford higher yields. However, no N-arylation product was obtained in the absence of PPAPM, which showed that the ligand could promote N-arylation of amines (entry 10 in Table 1). Further experiments showed that the catalyst system containing 10 mol% CuI and 20 mol% PPAPM relative to aniline was the optimal choice. Under our optimal conditions, proline[13] and *N,N,N′,N′*-tetramethylethylenediamine,[10] which are usually used as standard ligands in copper-catalyzed cross-coupling reactions, afforded 57 and 59% yield (entries 11 and 12 in Table 1), while our ligand PPAMP gave 70% yield (entry 9 in Table 1).

Coupling reactions of aryl halides with nitrogen-containing compounds were carried out under the optimal catalysis conditions: 10 mol% CuI as copper source, 20 mol% PPAPM as ligand, 2.2 equiv of $K_3PO_4$ as base, and DMF as solvent. We attempted to couple aryl halides with amines, amides, indole, and imidazole. The desired amination products of aryl bromides and iodides were obtained in good to excellent yields (Table 2), and even the sterically crowded 2,6-dimethylaniline gave satisfactory yields (entries 14 and 15 in Table 2). The results showed that the ligand could promote the conversion of all of the substrates to the corresponding arylamines, and the reactions could tolerate substituents with different electronic effects on both aryl halide and amine. Aryl iodides displayed higher reactivity than aryl bromides in the coupling reactions. For example, the coupling reaction of 1-bromo-4-iodobenzene with 4′-aminoacetophenone, 2-nitroaniline, or *N*-methylaniline (entries 16–18 in Table 2) yielded the target products **3o**, **3p**, and **3q** with a bromo substituent on the benzene ring.

Encouraged by the above promising results, the coupling reactions of phenylhydrazine with aryl halides were also carried out under our standard reaction conditions, and the corresponding N-arylation products were obtained in moderate to good yields (entries 28–33 in Table 2). The **A**-type products were obtained for reaction of aryl halides with substituents in *meta* or *para* position (entries 29–33 in Table 2), and the **B**-type product for *ortho*-substituted aryl halide (entry 28 in Table 2, Scheme 2), which was confirmed by $^1H$ NMR spectroscopy and is consistent with the literature.[20] In addition, the addition of an equivalent of LiCl[21] relative to phenylhydrazine to the reaction system could greatly improve the yields of the desired products (entries 31 and 33 in Table 2). However, the addition of one equivalent of NaCl could only slightly increase the yields (entries 32 and 33 in Table 2).

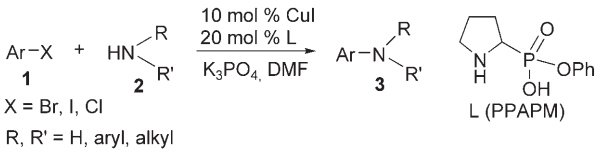
Coupling reactions of chlorobenzene with an amine, an amide, and an indole were also tested, and the chloride showed lower reactivity compared with bromides and iodides (entries 34–36 in Table 1). The results in Table 1 indicate the reactivity order of the aryl halides: iodides > bromides > chlorides.

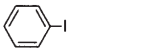
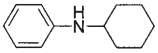
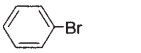
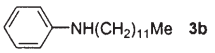
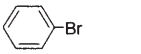
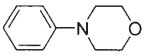
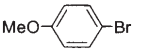
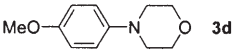
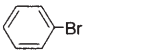
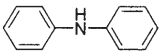
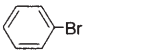
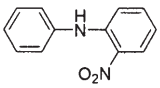
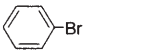
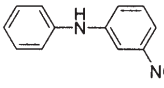
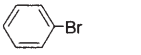
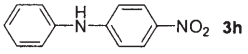
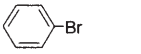
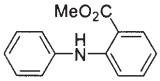
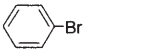
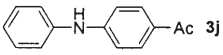
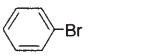
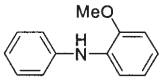
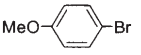
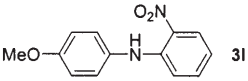
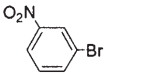
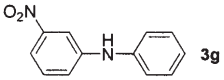
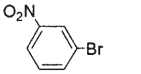
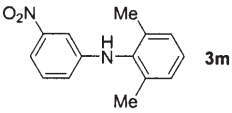
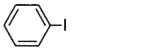
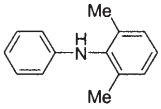
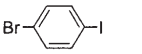
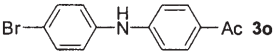
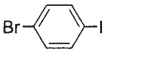
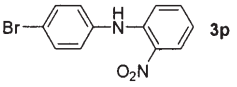
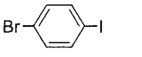
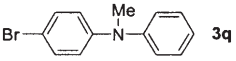
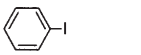
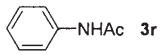
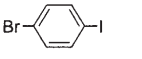
**Copper-catalyzed O-arylation reactions**: We performed a similar optimization process for copper-catalyzed O-arylation, and the optimal cross-coupling conditions were found (see Table 3). For example, bromobenzene (1 equiv) and phenol (1.5 equiv) were treated with $Cs_2CO_3$ (2.1 equiv), PPAPM (20 mol%), and CuI (10 mol%) in DMF (2.0 mL) at 110°C under nitrogen atmosphere, and diphenyl ether was isolated in 98% yield (entry 1 in Table 3), while it was obtained in 19 (entry 21 in Table 3) and 69% (entry 22 in Table 3) yield, respectively, in the absence of PPAPM and with proline as ligand. This shows that PPAPM can greatly improve the activity of the catalyst.

Coupling reactions of aryl halides with various substituted phenols and alcohols were carried out under the optimal catalysis conditions (10 mol% CuI as copper source, 20 mol% PPAPM as ligand, 2.2 equiv of $Cs_2CO_3$ as base, DMF as solvent), and the desired aryl ether products were obtained in good to excellent yields (Table 3). We found that the PPAPM could promote the conversion of all of the substrates to the corresponding aryl ethers, and aryl iodides showed higher reactivity than aryl bromides in the coupling reactions. For example, the coupling of 1-bromo-4-iodoben-

Table 2. Copper-catalyzed cross-coupling of aryl halides with amines, amides, indole, imidazole, and phenylhydrazine.[a]




| Entry | Aryl halide | Product | $T$ [°C] | $t$ [h] | Yield [%][b] |
|---|---|---|---|---|---|
| 1 |  |  **3a** | 90 | 16 | 95 |
| 2 |  |  **3b** | 90 | 24 | 87 |
| 3 |  |  **3c** | 90 | 30 | 91 |
| 4 |  |  **3d** | 90 | 30 | 87 |
| 5 |  |  **3e** | 110 | 36 | 77 |
| 6 |  |  **3f** | 110 | 30 | 90 |
| 7 |  |  **3g** | 110 | 30 | 83 |
| 8 |  |  **3h** | 110 | 30 | 86 |
| 9 |  |  **3i** | 110 | 30 | 84 |
| 10 |  |  **3j** | 110 | 36 | 85 |
| 11 |  |  **3k** | 110 | 36 | 82 |
| 12 |  |  **3l** | 110 | 36 | 80 |
| 13 |  |  **3g** | 100 | 30 | 89 |
| 14 |  |  **3m** | 100 | 30 | 75 |
| 15 |  |  **3n** | 110 | 30 | 82 |
| 16 |  |  **3o** | 110 | 24 | 91 |
| 17 |  |  **3p** | 90 | 20 | 98 |
| 18 |  |  **3q** | 110 | 36 | 71 |
| 19 |  |  **3r** | 110 | 30 | 89 |
| 20 |  |  **3s** | 100 | 20 | 94 |

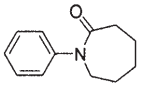
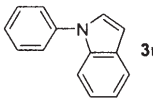
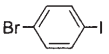
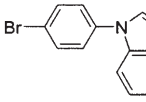
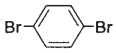
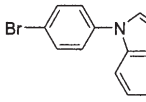
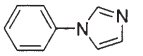
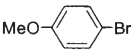
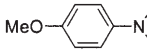
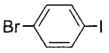
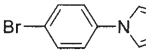
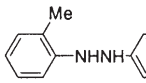
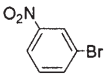
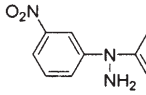
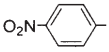
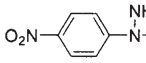
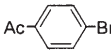
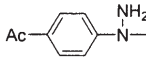
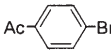
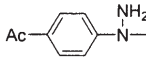
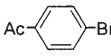
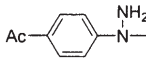
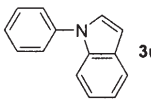
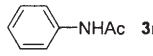
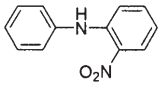
zene with phenol yielded the target product **5h** with a bromo substituent on the benzene ring (entry 10 in Table 3). We also tested reactions of alkyl alcohols with aryl halides, and aryl iodides showed higher reactivity than aryl bromides (entries 17–19 in Table 3). Coupling of chlorobenzene with phenol (entry 20 in Table 3), however, afforded the desired ether product in only 20% yield. Table 3 indicates the reactivity order of the aryl halides: iodides > bromides > chlorides, which is similar to the results in Table 2.

**Copper-catalyzed *P*-arylation reactions**: Phosphonates and functionalized monoarylphosphinic acids are valuable intermediates for the preparation of biological and medicinal compounds and synthetic intermediates, but copper-catalyzed methods to access them are currently limited.[18] We established optimal catalysis conditions for the copper-catalyzed formation of P–C bonds: 20 mol% CuI as copper source, 20 mol% PPAPM as ligand, $Cs_2CO_3$ or DMAP as base, and toluene or DMF as solvent.

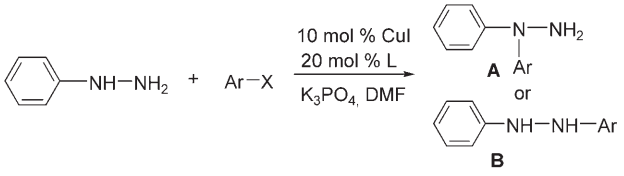
As shown in Table 4, the reactions with aryl iodides afforded moderate to good yields, but aryl bromides showed low reactivity (entries 13, 15, 17 in Table 4). However, reaction of aryl bromide with 2 equiv of KI for 12 h under the optimal condition provided the corresponding aryl iodide (Scheme 3), and when **7** was added to the resulting solution, the desired products was obtained in good yield (entries 14, 16, 18 in Table 4). Functionalized monoarylphosphinic acid **8k** was obtained by reaction of phenyl iodide with ammonium hypophosphite (entry 11 in Table 4); addition of an excess of phenyl iodide to the reaction system led to di-

Table 2. (Continued)

| Entry | Aryl halide | Product | $T$ [°C] | $t$ [h] | Yield [%][b] |
|---|---|---|---|---|---|
| 21 |  |  **3t** | 110 | 28 | 84 |
| 22 |  |  **3u** | 100 | 24 | 96 |
| 23 |  |  **3v** | 110 | 30 | 95 |
| 24 |  |  **3v** | 110 | 36 | 87 |
| 25 |  |  **3w** | 100 | 24 | 86 |
| 26 |  |  **3x** | 110 | 30 | 85 |
| 27 |  |  **3y** | 95 | 24 | 89 |
| 28 |  |  **3z** | 110 | 36 | 74[c] |
| 29 |  |  **3a'** | 110 | 36 | 77[c] |
| 30 |  |  **3b'** | 100 | 36 | 82[c] |
| 31 |  |  **3c'** | 110 | 36 | 84[c] |
| 32 |  |  **3c'** | 110 | 36 | 56[d] |
| 33 |  |  **3c'** | 110 | 36 | 51[e] |
| 34 |  |  **3u** | 120 | 48 | 39 |
| 35 |  |  **3r** | 120 | 48 | 33 |
| 36 |  |  **3f** | 120 | 48 | 32 |

[a] Reaction conditions: CuI (0.2 mmol), ligand (0.4 mmol), $K_3PO_4$ (4.4 mmol) in DMF (3 mL) under $N_2$. **1** (2 mmol for entries 1–15, 19, 21–22, 25–26 and 28–36; 3 mmol for other entries), **2** (3 mmol). [b] Yield of isolated product. [c] Additive (3 mmol of LiCl). [d] Additive (3 mmol of NaCl). [e] No salt additive.




Scheme 2. Copper-catalyzed reaction of phenylhydrazine with aryl halides.

substituted product **81** in 41% yield (entry 12 in Table 4).

## Conclusion

We have developed a general and efficient protocol for the formation of C–N, C–O, and P–C bonds by copper-catalyzed cross-coupling. Addition of the new and readily available bidentate PPAMP ligand could greatly promote the reactivity of the catalyst system. The versatile and efficient copper/ligand catalyst system is of widespread and practical application in cross-coupling reactions.

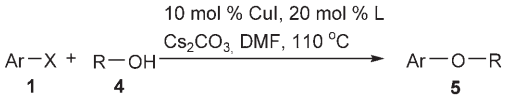
## Experimental Section

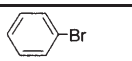
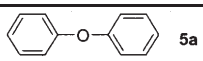
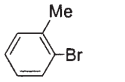
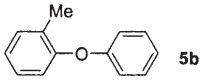
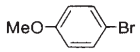
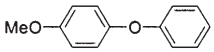
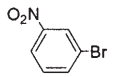
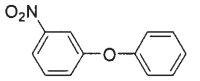
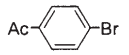
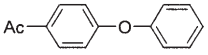
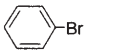
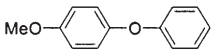
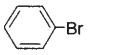
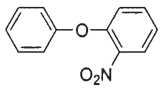
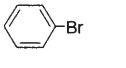
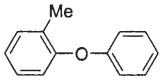
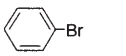
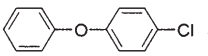
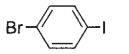
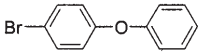
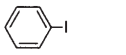
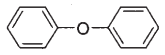
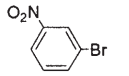
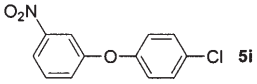
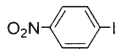
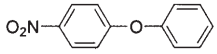
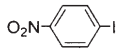
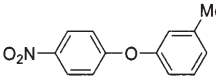
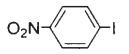
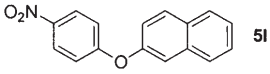
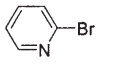
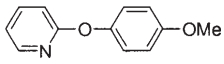
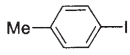
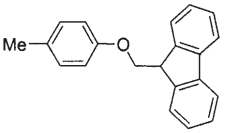
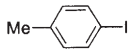
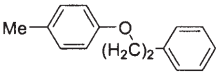
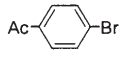
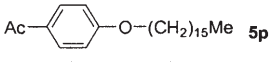
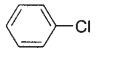
**General methods**: All reactions were carried out under nitrogen atmosphere. DMF was freshly distilled from $CaH_2$. $^1H$ and $^{13}C$ NMR spectra were recorded with tetramethylsilane and solvent as internal standard ($^1H$ NMR: TMS at $\delta = 0.00$ ppm, $CDCl_3$ at $\delta = 7.24$ ppm, DMSO at $\delta = 2.50$ ppm; $^{13}C$ NMR: $CDCl_3$ at $\delta = 77.0$ ppm). 85% aqueous $H_3PO_4$ was used as external reference for $^{31}P$ NMR spectra.

**Synthesis of pyrrolidine-2-phosphonic acid phenyl monoester hydrochloride (PPAPM)**: A mixture of 1-pyrroline trimer[19a] (15 mmol, 3.11 g) and diphenyl phosphite (45 mmol, 10.53 g) was heated under nitrogen atmosphere to give crude diphenyl pyrrolidine-2-phosphonate, which was dissolved in dry diethyl ether (100 mL). The resulting solution was filtered, and the filtrate was saturated with dry HCl gas. The precipitated diphenyl pyrrolidine-2-phosphonate hydrochloride was collected by filtration, washed with diethyl ether, and recrystallized from acetone[19b] to give the pure product as a white solid. Then the product (14 mmol, 4.75 g) was dissolved in $CH_3CN/H_2O$ (1/1; 25 mL) solution, and aqueous LiOH (1 M, 30 mL) was added dropwise.[19c] After 3 h, the mixture was extracted with $CH_2Cl_2$, the aqueous solution acidified with HCl (3 M) to pH 3 and evaporated, the residue dissolved in $CH_3OH$ and filtered, and the filtrate dried ($MgSO_4$), and evaporated to give the desired product as a white solid. Total yield 32% (3.80 g), m.p. 123–125 °C. $^{31}P$ NMR ($D_2O$, 121 MHz): $\delta = 11.97$. $^1H$ NMR ($D_2O$, 300 MHz): $\delta = 7.32$ (t, $J = 7.57$ Hz, 2H), 7.21 (t, $J = 7.57$ Hz, 1H), 7.07 (d, $J = 7.22$ Hz, 2H), 4.29–4.33 (m, 1H), 3.42–3.46 (m, 2H), 2.07–2.48 ppm (m, 4H); $^{13}C$ NMR ($D_2O$, 75 MHz): $\delta = 149.4$, 130.1, 120.8, 115.6, 54.0, 51.9, 26.8, 24.3 ppm; HR-ESI-MS: $[M+H]^+$ $m/z$ calcd for $C_{10}H_{15}NO_3P$: 228.0790; found: 228.0796.

Table 3. Copper-catalyzed cross-coupling of aryl halides with substituted phenols and alkyl alcohols.[a]




| Entry | Aryl halide | Product | *t* [h] | Yield [%][b] |
|---|---|---|---|---|
| 1 |  |  **5a** | 18 | 98 |
| 2 |  |  **5b** | 20 | 96 |
| 3 |  |  **5c** | 36 | 93 |
| 4 |  |  **5d** | 14 | 96 |
| 5 |  |  **5e** | 16 | 94 |
| 6 |  |  **5c** | 15 | 96 |
| 7 |  |  **5f** | 36 | 71 |
| 8 |  |  **5b** | 17 | 93 |
| 9 |  |  **5g** | 36 | 83 |
| 10 |  |  **5h** | 13 | 97 |
| 11 |  |  **5a** | 15 | 95 |
| 12 |  |  **5i** | 36 | 83 |
| 13 |  |  **5j** | 13 | 95 |
| 14 |  |  **5k** | 13 | 93 |
| 15 |  |  **5l** | 15 | 92 |
| 16 |  |  **5m** | 30 | 96 |
| 17 |  |  **5n** | 36 | 91 |
| 18 |  |  **5o** | 36 | 89 |
| 19 |  |  **5p** | 36 | 60 |
| 20 |  |  **5a** | 36 | 20 |
| 21 |  |  **5a** | 48 | 19[c] |
| 22 |  |  **5a** | 30 | 69[d] |

[a] Reaction conditions: aryl halide (2 mmol for entries 1–9 and 11–20, 3 mmol for entry 10), aryl phenol or alkyl alcohol (3 mmol), L (0.4 mmol), CuI (0.2 mmol), $Cs_2CO_3$ (4.4 mmol), DMF (3 mL) at 110 °C under $N_2$. [b] Yield of isolated product. [c] No ligand was used. [d] Proline was used instead of PPAPM.

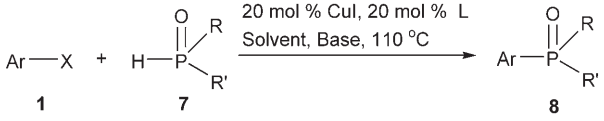
**General procedure for the preparation of compounds 3a–y**: A flask was charged with PPAPM hydrochloride (100 mg, 0.4 mmol) and potassium phosphate (607 mg, 4.4 mmol), evacuated and backfilled with nitrogen at low temperature. Aryl halide (2 mmol for entries 1–15, 19, 21, 22, 25, 26, and 34–36; 3 mmol for other entries in Table 2), and nitrogen-containing compound **2** (3 mmol), and DMF (3 mL) were added under nitrogen atmosphere. After 30 min, CuI (40 mg, 0.2 mmol) was added under nitrogen atmosphere. The flask was immersed in an oil bath, and the reaction mixture was stirred at the temperature and for the reaction time indicated in Table 1. The reaction mixture was cooled to room temperature, ethyl acetate (10 mL) was added, the resulting suspension was filtered, the filtrate was concentrated, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 20/1 to 2/1) to give the desired product.

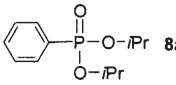
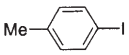
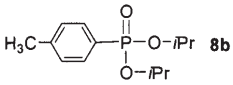
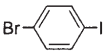
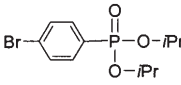
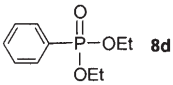
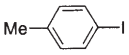
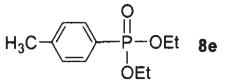
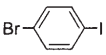
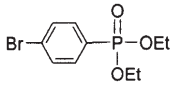
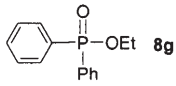
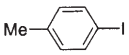
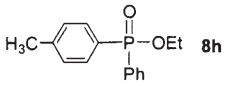
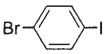
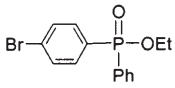
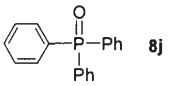
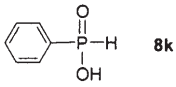
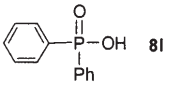
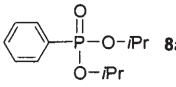
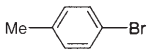
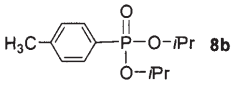
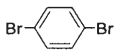
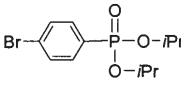
**General procedure for the preparation of compounds 3z, 3a′–c′**: A flask was charged with phenylhydrazine (2 mmol), salt (3 mmol, LiCl for entries 28–31, NaCl for entry 32, no additive for entry 33 in Table 2), and DMF (3 mL), evacuated and backfilled with nitrogen. After 1 h, PPAPM hydrochloride (100 mg, 0.4 mmol), potassium phosphate (607 mg, 4.4 mmol), and aryl halide (2 mmol) were added under nitrogen atmosphere at low temperature. After a further 30 min, CuI (40 mg, 0.2 mmol) was added. The flask was immersed in an oil bath, and the reaction mixture was stirred at the temperature and for the reaction time indicated in Table 1. The reaction mixture was cooled to room temperature, ethyl acetate (10 mL) was added, the resulting suspension was filtered, the filtrate was concentrated, and the residue was purified by column chromatography on silica gel (hexane/EtOAc 10/1 to 6/1) to give the desired product.

***N*-cyclohexylaniline (3a)**:[22] Colorless oil, yield 95% (333 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 7.16$ (t, $J = 7.74$ Hz, 2H), 6.67 (t, $J = 7.57$ Hz, 1H), 6.61 (d, $J = 7.91$ Hz, 2H), 3.75 (br s, 1H), 3.25–3.28 (m, 1H), 2.03 –2.08 (m, 2H), 1.74–1.79 (m, 2H), 1.63–1.67 (m, 1H), 1.13–1.42 ppm (m, 5H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta = 147.1$, 129.4, 117.3, 113.5, 52.0, 33.5, 26.0, 25.1 ppm; HR-EI-MS: $[M]^+$ *m*/*z* calcd for $C_{12}H_{17}N$: 175.1361; found: 175.1368.

***N*-dodecylaniline (3b)**:[23] Milk-white oil, yield 87% (455 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 7.18$ (t, $J =$

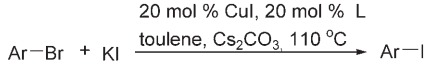
Table 4. Copper-catalyzed cross-coupling of aryl iodides with H-phosphonates and hypophosphite[a,b]




| Entry | 1 | 7 | Product | Base | Solvent | Yield [%][c] |
|---|---|---|---|---|---|---|
| 1 |  | $(i\mathrm{PrO})_2\mathrm{P(O)H}$ |  **8a** | $Cs_2CO_3$ | toluene | 73 |
| 2 |  | $(i\mathrm{PrO})_2\mathrm{P(O)H}$ |  **8b** | $Cs_2CO_3$ | toluene | 77 |
| 3 |  | $(i\mathrm{PrO})_2\mathrm{P(O)H}$ |  **8c** | $Cs_2CO_3$ | toluene | 81 |
| 4 |  | $(\mathrm{EtO})_2\mathrm{P(O)H}$ |  **8d** | $Cs_2CO_3$ | toluene | 75 |
| 5 |  | $(\mathrm{EtO})_2\mathrm{P(O)H}$ |  **8e** | $Cs_2CO_3$ | toluene | 73 |
| 6 |  | $(\mathrm{EtO})_2\mathrm{P(O)H}$ |  **8f** | $Cs_2CO_3$ | toluene | 78 |
| 7 |  |  |  **8g** | $Cs_2CO_3$ | toluene | 85 |
| 8 |  |  |  **8h** | $Cs_2CO_3$ | toluene | 79 |
| 9 |  |  |  **8i** | $Cs_2CO_3$ | toluene | 82 |
| 10 |  | $(\mathrm{Ph})_2\mathrm{P(O)H}$ |  **8j** | $Cs_2CO_3$ | toluene | 71 |
| 11 |  | $NH_3{\cdot}H_3PO_2$ |  **8k** | DMAP | DMF | 74 |
| 12 |  | $NH_3{\cdot}H_3PO_2$ |  **8l** | DMAP | DMF | 41 |
| 13<br>14 |  | $(i\mathrm{PrO})_2\mathrm{P(O)H}$ |  **8a** | $Cs_2CO_3$ | toluene | 25<br>70[d] |
| 15<br>16 |  | $(i\mathrm{PrO})_2\mathrm{P(O)H}$ |  **8b** | $Cs_2CO_3$ | toluene | 20<br>70[d] |
| 17<br>18 |  | $(i\mathrm{PrO})_2\mathrm{P(O)H}$ |  **8c** | $Cs_2CO_3$ | toluene | 24<br>70[d] |

[a] Reaction conditions: **1** (2 mmol), **7** (3 mmol), base (4.4 mmol) for entries 1–11; **1** (7 mmol), **7** (3 mmol), base (6.6 mmol) for entry 12; solvent (5 mL) at 110 °C for 36 h under $N_2$. [b] The resulting solution was evaporated, then the residue was diluted with water, washed with diethyl ether, acidified with $KHSO_4$ (1 M, saturated with NaCl); extracted with ethyl acetate for entries 11, 12. [c] Yield of isolated product. [d] After reaction of aryl bromide with 2 equiv of KI for 12 h under the optimal condition for entries 13, 15, 17, **7** was added to the resulting solution, and the reaction lasted for 36 h (entries 14, 16, 18).




Scheme 3. Copper-catalyzed reaction of aryl bromides with KI.

7.54 Hz, 2H), 6.70 (t, $J$=7.20 Hz, 1H), 6.62 (d, $J$=7.89 Hz, 2H), 3.11 (t, $J$=7.03 Hz, 2H), 1.67–1.65 (m, 2H), 1.29 (m, 18H), 0.91 ppm (t, $J$=6.00 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=148.7, 129.3, 117.2, 112.8, 44.1, 32.1, 29.7, 29.6, 29.5, 27.3, 22.8, 14.2 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{18}H_{31}N$: 261.2457; found: 261.2461.

**4-phenylmorpholine (3c)**:[24] White solid, yield 91% (297 mg), m.p. 51–54°C(lit.[24c] 54°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.29 (t, $J$=7.89 Hz, 2H), 6.88–6.96 (m, 3H), 3.88 (t, $J$=4.83 Hz, 4H), 3.17 ppm (t, $J$=4.83 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=151.2, 129.3, 120.7, 116.0, 67.0, 49.6 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{10}H_{13}NO$: 163.0997; found: 163.0990.

**4-(4-methoxyphenyl)morpholine (3d)**:[25] White solid, yield 87% (337 mg), m.p. 72–74°C (lit.[25b] 75°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=6.90 (d, $J$=9.29 Hz, 2H), 6.85 (d, $J$=9.29 Hz, 2H), 3.86 (t, $J$=4.82 Hz, 4H), 3.77 (s, 3H), 3.06 ppm (t, $J$=4.82 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=154.1, 145.7, 117.9, 114.6, 67.1, 55.7, 50.9 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{11}H_{15}NO_2$: 193.1103; found: 193.1110.

**Diphenylamine (3e)**:[26] White solid, yield 77% (261 mg), m.p. 52–53°C (lit.[26b] 54°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.24–7.29 (m, 4H), 7.08 (d, $J$=7.57 Hz, 4H), 6.93 ppm (t, $J$=7.22 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=143.1, 129.4, 121.2, 118.0 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{12}H_{11}N$: 169.0891; found: 169.0886.

***N*-(2-nitrophenyl)aniline (3f)**:[24] Yellow powder, yield 90% (386 mg), m.p. 72–74°C (lit.[24b] 75.5°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.50 (brs, 1H), 8.21 (dd, $J$=7.22, 1.38 Hz, 1H), 7.35–7.45 (m, 3H), 7.21–7.29 (m, 4H), 6.78 ppm (t, $J$=6.88 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=143.1, 138.7, 135.7, 132.3, 129.7, 126.7, 125.7, 124.4, 117.5, 116.0 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{12}H_{10}N_2O_2$: 214.0742; found: 214.0748.

***N*-(3-nitrophenyl)aniline (3g)**:[27] White solid, yield 83% (356 mg), m.p. 85–87°C (lit.[27] 89°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.84 (s, 1H), 7.69 (d, $J$=7.84 Hz, 1H), 7.29–7.38 (m, 4H), 7.14 (d, $J$=8.25 Hz, 2H), 7.08 (t, $J$=7.57 Hz, 1H), 5.90 ppm (brs, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=145.2, 141.0, 140.2, 130.1, 129.8, 123.3, 121.9, 120.0, 114.8, 110.4 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{12}H_{10}N_2O_2$: 214.0742; found: 214.0750.

***N*-(4-nitrophenyl)aniline (3h)**:[27] Yellow powder, yield 86% (369 mg), m.p. 132–135°C (lit.[27] 131°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=8.12 (d, $J$=9.27 Hz, 2H), 7.39 (t, $J$=7.56 Hz, 2H), 7.16–7.22 (m, 3H), 6.94 (d, $J$=9.27 Hz, 2H), 6.37 ppm (brs, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=150.3, 139.8, 139.6, 129.8, 126.3, 124.8, 122.0, 113.8 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{12}H_{10}N_2O_2$: 214.0742; found: 214.0747.

**Methyl 2-(phenylamino)benzoate (3i)**:[24] White solid, yield 84% (382 mg), m.p. 54–56°C (lit.[24a] 52–54°C). $^1$H NMR ($CDCl_3$, 600 MHz): $\delta$=9.46 (br, 1H), 7.95 (dd, $J$=8.25, 1.37 Hz, 1H), 7.33 (t, $J$=7.91 Hz, 2H), 7.29 (td, $J$=6.87, 1.37 Hz, 1H), 7.23–7.25 (m, 3H), 7.08 (t, $J$=7.56 Hz, 1H), 6.71 (t, $J$=7.56 Hz, 1H), 3.88 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 150 MHz): $\delta$=169.0, 148.0, 140.9, 134.2, 131.7, 129.5, 123.7, 122.6, 117.2, 114.1, 112.0, 51.9. 51.9 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{14}H_{13}NO_2$: 227.0946; found: 227.0951.

**1-(4-phenylamino)phenyl methyl ketone (3j)**:[28] White solid, yield 85% (359 mg), m.p. 105–106°C (lit.[28] 106°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.79 (dd, $J$=8.94, 1.72 Hz, 1H), 7.32 (m, 3H), 7.14 (d, 4H), 6.98 (dd, $J$=8.60, 1.72 Hz, 1H), 2.52 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=196.5, 152.1, 146.4, 129.9, 129.6, 125.9, 124.6, 119.6, 26.2 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{14}H_{13}NO$: 211.0997; found: 211.0995.

***N*-(2-methoxyphenyl)aniline (3k)**:[26] Yellow oil, yield 82% (327 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.23–7.28 (m, 3H), 7.13 (d, $J$=7.91 Hz, 2H), 6.92 (t, $J$=7.40 Hz, 1H), 6.84–6.53 (m, 3H), 6.14 (brs, 1H), 3.85 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=148.4, 142.9, 133.1, 129.4, 121.3, 120.9, 120.0, 118.7, 114.8, 110.7, 55.7 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{13}H_{13}NO$: 199.0997; found: 199.0993.

**4-Methoxy-*N*-(2-nitrophenyl)aniline (3l)**:[29] Yellow solid, yield 80% (391 mg), m.p. 87–88°C (lit.[29a] 87–88°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.41 (brs, 1H), 8.19 (d, $J$=8.60 Hz, 1H), 7.32 (t, $J$=7.91 Hz, 1H), 7.20 (d, $J$=8.60 Hz, 2H), 7.00 (d, $J$=8.94 Hz, 1H), 6.96 (dd, $J$=8.60, 1.72 Hz, 2H), 6.71 (t, $J$=7.74 Hz, 1H), 3.84 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=157.9, 144.5, 135.7, 132.4, 131.2, 127.1, 126.6, 116.8, 115.7, 114.9, 55.5 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{13}H_{12}N_2O_3$: 244.0848; found: 244.0842.

***N*-(2,6-dimethylphenyl)-3-nitroaniline (3m)**:[25] Yellow solid, yield 75% (363 mg), m.p. 79–83°C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.71 (d, $J$=8.58 Hz, 1H), 7.21 (s, 1H), 6.99–7.08 (m, 5H), 6.40 (s, 1H), 1.98 ppm (s, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=158.9, 141.3, 137.6, 129.3, 128.6, 128.0, 125.6, 124.5, 124.3, 113.6, 18.3 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{14}H_{14}N_2O_2$: 242.1055; found: 242.1051.

***N*-(2,6-dimethylphenyl)aniline (3n)**:[25] Slightly yellow oil, yield 82% (324 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.27 (t, $J$=8.08 Hz, 2H), 7.01–7.17 (m, 3H), 6.90 (d, $J$=7.91 Hz, 2H), 6.74 (t, $J$=7.22 Hz, 1H), 2.21 ppm (s, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=146.4, 135.9, 129.6, 129.3, 128.6, 118.3, 117.7, 113.6, 18.5 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{14}H_{15}N$: 197.1204; found: 197.1210.

**4-(4-bromophenylamino)phenyl methyl ketone (3o)**:[30] White solid, yield 91% (529 mg), m.p. 114–116°C (lit.[30] 114–116°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.82 (d, $J$=8.60 Hz, 2H), 7.60 (d, $J$=8.60 Hz, 2H), 7.42 (d, $J$=8.94 Hz, 2H), 7.02 (d, $J$=8.94 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=196.6, 145.4, 138.8, 132.9, 131.0, 130.1, 127.1, 121.0, 117.6, 26.4 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{14}H_{12}BrNO$: 289.0102; found: 289.0108.

**4-Bromo-*N*-(2-nitrophenyl)aniline (3p)**:[29] Yellow powder, yield 98% (575 mg), m.p. 166–168°C (lit.[29b] 167°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=9.39 (brs, 1H), 8.20 (dd, $J$=8.23, 1.35 Hz, 1H), 7.52 (d, $J$=8.61 Hz, 2H), 7.39 (t, $J$=7.22 Hz, 1H), 7.15–7.21 (m, 3H), 6.81 ppm (t, $J$=8.23 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=142.5, 138.9, 135.9, 132.9, 126.9, 125.8, 118.5, 118.2, 116.1. 116.1 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{12}H_9BrN_2O_2$: 291.9847; found: 291.9852.

**4-Bromo-*N*-methyl-*N*-phenylaniline (3q)**:[31] Yellow oil, yield 71% (372 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.41 (d, $J$=8.94, 2H), 7.33 (dd, $J$=7.89, 7.56 Hz, 2H), 7.11 (t, $J$=7.56 Hz, 1H), 6.99 (d, $J$=7.89 Hz, 2H), 6.87 (d, $J$=8.94 Hz, 2H), 2.85 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=156.7, 138.8, 132.8, 130.0, 120.9, 120.6, 119.2, 115.7, 41.8 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{13}H_{12}BrN$: 261.0153; found: 261.0151.

***N*-phenylacetamide (3r)**:[32] White powder, yield 89% (241 mg), m.p. 161–164°C (lit.[32] 163°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.50 (d, $J$=7.89 Hz, 2H), 7.26–7.33 (dd, $J$=7.89, 7.56 Hz, 2H), 7.07–7.12 (dd, $J$=7.57, 7.22 Hz, 1H), 2.16 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=168.5, 138.0, 129.0, 124.4, 120.0, 24.6. 24.6 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_8H_9NO$: 135.0684; found: 135.0681.

***N*-(4-bromophenyl)acetamide (3s)**:[33] White powder, yield 94% (403 mg), m.p. 166–169°C (lit.[33] 168°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=8.15 (brs, 1H), 7.22–7.57 (m, 4H), 2.13 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=168.4, 138.0, 132.0, 121.7, 121.5, 24.7; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_8H_8BrNO$: 212.9789; found: 212.9785.

***N*-Phenyl-ε-caprolactam (3t)**:[34] White powder, yield 84% (318 mg), m.p. 75–78°C (lit.[34] 72–73°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.37 (dd, $J$=8.58, 1.38 Hz, 2H), 7.19–7.24 (m, 3H), 3.74–3.76 (m, 2H), 2.69–2.71 (m, 2H), 1.81–1.83 ppm (m, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=175.6, 144.7, 129.2, 126.5, 126.3, 53.1, 37.8, 30.0, 29.0, 23.6 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{12}H_{15}NO$: 189.1154; found: 189.1161.

***N*-phenylindole (3u)**:[35] Oil, yield 96% (371 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.68 (dd, 1.72 Hz, $J$=8.60), 7.55 (d, $J$=8.26 Hz, 1H), 7.47–7.49 (m, 4H), 7.31–7.35 (m, 2H), 7.15–7.18 (m, 2H), 6.67 ppm (d, $J$=8.26 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$=140.0, 136.0, 129.7, 129.5, 128.1, 126.6, 124.5, 122.5, 121.3, 120.5, 110.6, 103.7 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{14}H_{11}N$: 193.0891; found: 193.0887.

***N*-(4-bromophenyl)indole (3v)**:[35] Yellow solid, yield 95% (518 mg), m.p. 64–65°C (lit.[35] 64–65°C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$=7.63 (d, $J$=7.2 Hz, 1H), 7.47–7.49 (m, 3H), 7.43 (d, $J$=8.58 Hz, 1H), 7.16–7.22 (m, 2H), 7.13–7.15 (m, 2H), 6.61 ppm (d, $J$=3.09 Hz, 1H); $^{13}$C NMR

($CDCl_3$, 75 MHz): $\delta$ = 139.1, 135.9, 133.0, 129.7, 127.8, 125.9, 123.0, 121.6, 121.0, 119.9, 110.7, 104.5. 104.5 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{14}H_{10}BrN$: 270.9997; found: 270.9992.

***N*-phenylimidazole (3w)**:[36] Slightly yellow oil, yield 86% (248 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.83 (s, 1H), 7.24–7.29 (m, 2H), 7.07–7.09 (m 2H), 6.93 (t, $J$ = 8.64 Hz, 1H), 6.68–6.70 ppm (m, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 139.7, 135.6, 132.5, 130.2, 127.5, 121.8, 112.8 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_9H_8N_2$: 144.0687; found: 144.0683.

***N*-(4-methoxyphenyl)imidazole (3x)**:[36] Colorless oil, yield 85% (296 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.78 (s, 1H), 7.28 (dd, $J$ = 8.94, 1.72 Hz, 2H), 7.27 (s, 2H), 6.98 (dd, $J$ = 8.94, 1.72 Hz, 2H), 3.84 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 159.0, 136.0, 130.8, 130.0, 123.3, 118.8, 115.0, 55.7. 55.7 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{10}H_{10}N_2O$: 174.0793; found: 174.0786.

***N*-(4-bromophenyl)imidazole (3y)**:[37] Yellow solid, yield 89% (397 mg), m.p. 115–116 °C (lit.[37] 119–120 °C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.83 (s, 1H), 7.63 (m, 2H), 7.03–7.37 ppm (m, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 139.5, 133.5, 130.0, 123.6, 121.0, 119.2, 91.8. 91.8 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_9H_7BrN_2$: 221.9793; found: 221.9789.

**2-Phenyl-1-(2-methylphenyl)hydrazine (3z)**:[38] Slightly yellow oil, yield 74% (294 mg). $^1$H NMR (DMSO, 300 MHz): $\delta$ = 7.23–7.28 (m, 3H), 7.12–7.14 (m, 2H), 6.85–6.92 (m, 4H), 6.16 (s, 1H), 5.71 (s, 1H), 2.40 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 148.4, 142.9, 133.1, 129.4, 125.1, 124.3, 121.3, 120.9, 114.8, 110.7, 17.7. 17.7 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{13}H_{14}N_2$: 198.1157; found: 198.1155.

**1-Phenyl-1-(3-nitrophenyl)hydrazine (3a′)**. Yellow solid, yield 77% (353 mg), m.p. 77–80 °C. $^1$H NMR (DMSO, 300 MHz): $\delta$ = 7.84 (s, 1H), 7.69 (d, $J$ = 7.84 Hz, 1H), 7.29–7.38 (m, 4H), 7.14 (d, $J$ = 8.25 Hz, 2H), 7.08 (t, $J$ = 7.57 Hz, 1H), 2.31 ppm (s, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 155.3, 152.5, 147.6, 132.5, 129.7, 120.2, 116.1, 113.1, 110.5, 105.6 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_{11}N_3O_2$: 229.0851; found: 229.0847.

**1-Phenyl-1-(4-nitrophenyl)hydrazine (3b′)**:[39] White solid, yield 82% (376 mg), m.p. 89–92 °C. $^1$H NMR (DMSO, 300 MHz): $\delta$ = 8.12 (d, $J$ = 9.27 Hz, 2H), 7.39 (t, $J$ = 7.56 Hz, 2H), 7.16–7.22 (m, 3H), 6.94 (d, $J$ = 9.27 Hz, 2H), 6.37 (brs, 1H), 2.20 ppm (s, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 157.1, 149.7, 138.4, 129.2, 123.0, 120.0, 118.2, 112.8 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_{11}N_3O_2$: 229.0851; found: 229.0856.

**1-Phenyl-1-(4-acetylphenyl)hydrazine (3c′)**: White solid, yield 84% (380 mg), m.p. 80–85 °C. $^1$H NMR (DMSO, 300 MHz): $\delta$ = 7.74 (d, $J$ = 8.58 Hz, 2H), 7.57 (d, $J$ = 8.58 Hz, 2H), 7.23–7.25 (m, 4H), 6.78–6.80 (m, 1H), 2.53 (s, 2H), 2.24 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 200.7, 155.8, 150.2, 131.8, 130.5, 126.4, 120.7, 115.4, 113.1, 29.6 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{14}H_{14}N_2O$: 226.1106; found: 226.1110.

**General procedure for the preparation of compounds 5a–p**: Aryl halide (2 mmol for entries 1–9 and 11–20, 3 mmol for entry 10 in Table 3), phenol (3 mmol), and PPAPM hydrochloride (104 mg, 0.4 mmol) were added to a flask with $Cs_2CO_3$ (1432 mg, 4.4 mmol) and DMF (3 mL), the mixture was stirred for 30 min at room temperature under nitrogen atmosphere, and CuI (40 mg, 0.2 mmol) was added to the flask. The flask was immersed in an oil bath, and the reaction mixture was stirred at 110 °C for the reaction time indicated in Table 2. The reaction mixture was then allowed to cool to room temperature, diluted with ethyl acetate (10 mL) and filtered, and the filtrate was concentrated under vacuum to give the crude product. Purification by column chromatography on silica gel (hexane/EtOAc 15/1 to 100% hexane) afforded the desired pure product.

**Diphenyl ether (5a)**:[40] Colorless oil, yield 98% (333 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.33 (t, $J$ = 7.89 Hz, 4H), 7.09 (t, $J$ = 7.89 Hz, 2H), 7.01 ppm (d, $J$ = 8.25 Hz, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 157.2, 129.7, 123.2, 118.9 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_{10}O$: 170.0732; found: 170.0738.

**2-Methylphenyl phenyl ether (5b)**:[21] Colorless oil, yield 96% (353 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.31 (q, 3H), 7.19 (t, $J$ = 7.56 Hz, 1H), 7.06 (q, 2H), 6.93 ppm (d, $J$ = 7.89 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 158.0, 154.6, 131.6, 129.8, 127.3, 124.1, 122.4, 119.9, 117.4, 29.9 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_{10}O$: 184.0888; found: 184.0881.

**4-Methoxyphenyl phenyl ether (5c)**:[41] Colorless oil, yield 93% (372 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.28 (t, $J$ = 7.56 Hz, 2H), 7.05–6.85 ppm (m, 7H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 158.6, 156.0, 150.2, 129.7, 122.5, 121.0, 117.7, 115.0, 55.7 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{13}H_{12}O_2$: 200.0837; found: 200.0842.

**3-Nitrophenyl phenyl ether (5d)**:[42] Colorless oil or white solid, yield 96% (413 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = $\delta$7.91 (d, $J$ = 9.27 Hz, 1H), 7.78 (t, $J$ = 2.07 Hz, 1H), 7.46–7.20 (m, 4H), 7.05 ppm (d, $J$ = 7.56 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 158.7, 155.6, 149.4, 130.4, 124.9, 124.2, 119.9, 117.7, 112.9 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_{10}O$: 215.0582; found: 215.0577.

**4-Phenoxyacetophenone (5e)**:[43] White solid, yield 94% (399 mg), m.p. 49–51 °C (lit.[42] 50–51 °C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.94 (dd, $J$ = 8.91, 1.38 Hz, 2H), 7.37–7.42 (m, 2H), 7.18–7.26 (m, 1H), 6.98–7.08 (m, 4H), 2.57 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 196.8, 162.1, 155.6, 132.0, 130.7, 130.1, 124.7, 120.3, 117.4, 26.5 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_{12}O_2$: 212.0837; found: 212.0832.

**2-Nitrophenyl phenyl ether (5f)**:[44] White solid, yield 93% (400 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.34 (dd, $J$ = 8.58, 1.35 Hz, 1H), 7.87 (dd, $J$ = 8.25, 2.31 Hz, 1H), 7.37–7.45 (m, 3H), 7.21–7.29 ppm (m, 4H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 157.4, 149.9, 139.8, 134.4, 129.8, 123.4, 122.5, 122.3, 118.2, 117.5 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_{19}NO_3$: 215.0582; found: 215.0576.

**4-Chlorophenyl phenyl ether (5g)**:[45] Colorless oil, yield 83% (339 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.40 (d, $J$ = 8.91 Hz, 2H), 7.32 (m, 2H), 7.10 (m, 1H), 6.98 (td, $J$ = 8.58, 1.05 Hz), 6.87 ppm (t, $J$ = 8.94, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 157.6, 156.7, 132.8, 130.0, 126.7, 121.0, 120.6, 119.2 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_9ClO$: 204.0342; found: 204.0338.

**4-Bromophenyl phenyl ether (5h)**:[46]Colorless oil, yield 97% (481 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.40 (d, $J$ = 8.91 Hz, 2H), 7.32 (m, 2H), 7.10 (m, 1H), 6.98 (td, $J$ = 8.58, 1.05 Hz), 6.87 ppm (t, $J$ = 8.94, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 156.7, 138.8, 132.8, 130.0, 123.9, 120.6, 119.2, 115.8 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_9BrO$: 247.9837; found: 247.9831.

**3-Nitrophenyl 4-chlorophenyl ether (5i)**:[45] Colorless thick oil, yield 83% (413 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.96 (d, $J$ = 9.27 Hz, 2H), 7.80 (t, $J$ = 2.40 Hz, 1H), 7.50 (t, $J$ = 8.25 Hz, 1H), 7.38–7.35 (m, 3H), 7.00 ppm (d, $J$ = 6.54 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 158.2, 154.3, 149.4, 130.6, 124.3, 121.1, 118.1, 113.0 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_8ClNO_3$: 249.0193; found: 249.0186.

**4-Nitrophenyl phenyl ether (5j)**:[47] Yellow solid, yield 95% (409 mg). m.p. 58–60 °C (lit.[46] 60 °C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.17 (d, $J$ = 9.27 Hz, 2H), 7.42 (t, $J$ = 7.89 Hz, 2H), 7.25 (t, $J$ = 7.56 Hz, 1H), 7.08 (d, $J$ = 7.82 Hz, 2H), 7.00 ppm (d, $J$ = 8.85 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.5, 154.8, 142.7, 130.4, 126.0, 125.5, 120.6, 117.2 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_9NO_3$: 215.0582; found: 215.0574.

**3-Methylphenyl 4-nitrophenyl ether (5k)**:[48] Yellow solid, yield 93% (426 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.11 (d, $J$ = 9.27 Hz, 2H), 7.22 (m, 1H), 6.99–6.79 ppm (m, 5H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.6, 154.8, 142.6, 140.8, 130.1, 126.3, 126.0, 121.2, 117.6, 117.2, 21.4 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{13}H_{11}NO_3$: 229.0739; found: 229.0731.

**4-Nitrophenyl 2-naphthyl ether (5l)**:[49] Yellow solid, yield 92% (488 mg). m.p. 137–140 °C (lit.[48] 137–138 °C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.23 (d, 2H), 7.91 (t, 2H), 7.78 (d, 1H), 7.52 (m, 3H), 7.25 (dd, 1H), 7.06 ppm (d, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 163.5, 152.4, 142.9, 134.3, 131.2, 130.7, 128.0, 127.5, 127.1, 126.1, 125.9, 120.3, 117.4, 117.1 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{16}H_{11}NO_3$: 265.0739; found: 265.0730.

**2-(4-Methoxyphenoxy)pyridine (5m)**:[50] Colorless oil, yield 96% (386 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 8.16 (d, $J$ = 3.09 Hz, 1H), 7.61 (td, $J$ = 8.91, 2.04 Hz, 1H), 7.06 (d, $J$ = 9.27 Hz, 2H), 6.72–6.92 (m, 4H), 3.77 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta$ = 164.4, 156.7, 147.7, 147.5, 139.5, 122.5, 118.2, 114.9, 111.1, 55.7 ppm; HR-EI-MS: $[M]^+$ *m/z* calcd for $C_{12}H_{11}NO_2$: 201.0790; found: 201.0784.

**9-Fluorene 4-methylphenyl ether (5n)**: White solid, yield 91% (521 mg), m.p. 59–65 °C. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ = 7.77 (d, $J$ = 7.56 Hz, 2H), 7.61 (d, $J$ = 7.56 Hz, 2H), 7.32–7.40 (m, 4H), 7.08 (d, $J$ = 7.56 Hz, 2H),

4.13 (t, $J=6.36$ Hz, 1H), 4.04 (d, $J=6.36$ Hz, 2H), 2.20 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=156.1$, 144.4, 141.8, 128.8, 127.7, 127.4, 127.2, 124.8, 120.2, 116.4, 72.0, 56.1, 24.5 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{21}H_{18}O$: 286.1358; found: 286.1352.

**4-Methylphenyl phenylethyl ether (5o)**:[51] Colorless oil, yield 89% (378 mg). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.56$ (d, $J=9.27$ Hz, 2H), 7.39 (t, $J=7.89$ Hz, 2H), 7.16–7.22 (m, 3H), 6.94 (d, $J=9.27$ Hz, 2H), 4.20 (t, $J=6.71$ Hz, 2H), 2.91 (t, $J=6.54$ Hz, 2H), 2.20 ppm (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=154.8$, 140.2, 130.4, 129.6, 128.9, 127.8, 126.0, 115.3, 59.2, 32.9, 23.0 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{15}H_{16}O$: 212.1201; found: 212.1207.

**4-Hexadecyloxyacetophenone (5p)**:[52] White solid, yield 60% (432 mg), m.p. 49–53 °C (lit.[16] 51–54 °C). $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.93$ (dd, $J=8.94$, 1.38 Hz, 2H), 7.00 (d, $J=8.58$ Hz, 2H), 4.02 (t, $J=6.53$ Hz, 2H), 2.57 (s, 3H), 1.78–1.82 (m, 2H), 1.26 (br, 26H), 0.88 ppm (t, $J=6.53$ Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=198.2$, 160.3, 129.7, 128.4, 113.4, 68.6, 32.3, 29.5, 28.7, 27.0, 15.2 ppm; HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{24}H_{40}O_2$: 360.3028; found: 360.3023.

**General procedure for the preparation of compounds 8a–j**: Aryl halide (2 mmol), phosphonate (3 mmol), and PPAPM hydrochloride (104 mg, 0.4 mmol) were added to a flask with $Cs_2CO_3$ (1432 mg, 4.4 mmol) and toluene (3 mL), the mixture was stirred for 30 min at room temperature under nitrogen atmosphere, and CuI (76.4 mg, 0.4 mmol) was added to the flask. The flask was immersed in an oil bath, and the reaction mixture was stirred at 110 °C for 36 h. The reaction mixture was then allowed to cool to room temperature, diluted with diethyl ether (10 mL), and filtered, and the filtrate was concentrated under vacuum. Purification by column chromatography on silica gel (hexane/chloroform 4/1 to 100% chloroform) afforded the desired pure product.

**General procedure for the preparation of compounds 8k and 8l**: Aryl halide (2 mmol for entry 11 and 7 mmol for entry 12 in Table 4), ammonium hypophosphite[53] (3 mmol), and PPAPM hydrochloride (104 mg, 0.4 mmol) were added to a flask with DMAP (806 mg, 6.6 mmol) and DMF (3 mL), the mixture was stirred for 30 min at room temperature under nitrogen atmosphere, and CuI (76.4 mg, 0.4 mmol) was added to the flask. The flask was immersed in an oil bath, and the reaction mixture was stirred at 110 °C for 36 h. The reaction mixture was then allowed to cool to room temperature and evaporated, the residue diluted with water (10 mL), and the solution washed with $Et_2O$ and acidified with $KHSO_4$ (1 M, satd with NaCl). The resulting aqueous phase was extracted with ethyl acetate (3 mL × 4). The organic phases were combined, dried with $MgSO_4$, filtered, and concentrated under vacuum to give the pure product.

**Diisopropyl phenylphosphonate (8a)**:[54] Oil, yield 73% (353 mg). $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=17.07$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.83$ (t, $J=7.58$ Hz, 1H), 7.50 (d, $J=7.89$ Hz, 2H), 7.26–7.33 (m, 2H), 3.92–3.95 (m, 2H), 1.36 ppm (d, $J=7.56$ Hz, 12H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=136.3$ ($J=5.7$ Hz), 134.0 ($J=159$ Hz), 132.1 ($J=2.9$ Hz), 129.2 ($J=2.2$ Hz), 71.3 ($J=5.7$ Hz), 24.4 ppm ($J=7.9$ Hz); HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{12}H_{19}O_3P$: 242.1072; found: 242.1077.

**Diisopropyl (4-methylphenyl)phosphonate (8b)**:[54] Oil, yield 77% (388 mg). $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=16.64$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.62$ (d, $J=8.94$ Hz, 2H), 7.20 (d, $J=8.94$ Hz, 2H), 3.48–3.60 (m, 1H), 2.24 (s, 3H), 1.17 ppm (d, $J=7.56$ Hz, 12H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=142.5$ ($J=13.6$ Hz), 135.0 ($J=13.6$ Hz), 131.8 ($J=162.1$ Hz), 129.9 ($J=13.6$ Hz), 71.3 ($J=5.7$ Hz), 25.0, 24.4 ppm ($J=7.9$ Hz); HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{13}H_{21}O_3P$: 256.1228; found: 256.1222.

**Diisopropyl (4-bromophenyl)phosphonate (8c)**:[55] Oil, yield 81% (518 mg). $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=17.34$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.62$ (d, $J=8.94$ Hz, 2H), 7.20 (d, $J=8.94$ Hz, 2H), 3.48–3.55 (m, 1H), 1.17 ppm (d, $J=7.56$ Hz, 12H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=137.2$ ($J=11.5$ Hz), 133.4 ($J=188.6$ Hz), 131.2 ($J=17.2$ Hz), 127.0 ($J=4.3$ Hz), 71.3 ($J=5.7$ Hz), 24.5 ppm ($J=7.9$ Hz); HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{12}H_{18}BrO_3P$: 320.0177; found: 320.0173.

**Diethyl phenylphosphonate (8d)**:[54] Oil, yield 75% (321 mg). $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=16.59$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.83$ (t, $J=7.58$ Hz, 1H), 7.50 (d, $J=7.89$ Hz, 2H), 7.26–7.33 (m, 2H), 3.77 (m, 4H), 1.18 ppm (t, $J=7.2$ Hz, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=135.1$ ($J=12.9$ Hz), 132.5 ($J=176.4$ Hz), 132.1 ($J=4.5$ Hz), 128.1 ($J=17.5$ Hz), 61.8 ($J=5.7$ Hz), 16.3 ppm ($J=5.7$ Hz); HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{10}H_{15}O_3P$: 214.0759; found: 214.0752.

**Diethyl (4-methylphenyl)phosphonate (8e)**:[54] Oil, yield 73% (333 mg). $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=16.51$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.62$ (d, $J=8.94$ Hz, 2H), 7.20 (d, $J=8.94$ Hz, 2H), 3.76–3.78 (m, 4H), 2.24 (s, 3H), 1.17 ppm (t, $J=7.2$ Hz, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=142.1$ ($J=4.3$ Hz), 134.9 ($J=10.0$ Hz), 130.7 ($J=188.6$ Hz), 129.1 ($J=16.5$ Hz), 61.8 ($J=5.7$ Hz), 22.2, 16.3 ppm ($J=5.7$ Hz); HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{11}H_{17}O_3P$: 228.0915; found: 228.0920.

**Diethyl (4-bromophenyl)phosphonate (8f)**:[56] Oil, yield 78% (456 mg). $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=16.70$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.62$ (d, $J=8.94$ Hz, 2H), 7.20 (d, $J=8.94$ Hz, 2H), 3.84–3.86 (m, 4H), 1.17 ppm (t, $J=7.2$ Hz, 6H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=133.3$ ($J=10.1$ Hz), 131.7 ($J=16.5$ Hz), 129.8 ($J=185.0$ Hz), 127.5 ($J=3.9$ Hz), 61.8 ($J=5.7$ Hz), 16.3 ppm ($J=5.7$ Hz); HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{10}H_{14}BrO_3P$: 291.9864; found: 291.9868.

**Ethyl diphenylphosphinate (8g)**:[57] Oil, yield 85% (418 mg). $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=19.48$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.75$ (dd, $J=7.56$, 1.38 Hz, 4H), 7.58 (d, $J=7.56$ Hz, 4H), 4.06 (q, $J=7.56$ Hz, 2H), 1.38 ppm (t, $J=7.56$ Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=132.6$ ($J=10.0$ Hz), 131.1 ($J=142.0$ Hz), 129.0 ($J=16.5$ Hz), 127.6 ($J=4.5$ Hz), 59.5 ($J=5.7$ Hz), 16.3 ppm ($J=5.7$ Hz); HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{14}H_{15}O_2P$: 246.0810; found: 246.0807.

**Ethyl (4-methylphenyl)phenylphosphinate (8h)**:[58] Oil, yield 79% (411 mg). $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=19.91$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.74$ (td, $J=7.56$, 1.38 Hz, 2H), 7.58 (d, $J=7.56$ Hz, 2H), 7.39–7.45 (m, 1H), 6.90–6.98 (m, 4H), 4.06 (q, $J=7.56$ Hz, 2H), 2.16 (s, 3H), 1.28 ppm (t, $J=7.56$ Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=141.2$ ($J=4.3$ Hz), 131.9 ($J=10.0$ Hz), 131.8 ($J=3.6$ Hz), 131.7 ($J=172.7$ Hz), 129.0 ($J=17.1$ Hz), 127.2 ($J=182.1$ Hz), 61.8 ($J=5.7$ Hz), 21.5, 16.3 ppm ($J=5.7$ Hz); HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{15}H_{17}O_2P$: 260.0966; found: 260.0969.

**Ethyl (4-bromophenyl)phenylphosphinate (8i)**: Oil, yield 82% (531 mg). $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=20.07$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.60$ (d, $J=8.91$ Hz, 2H), 7.49–7.54 (m, 2H), 7.38–7.43 (m, 1H), 7.18 (dd, $J=8.58$, 1.05 Hz, 2H), 7.06 (d, $J=8.94$, 2H), 4.06 (m, 2H), 1.28 ppm (t, $J=7.56$ Hz, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=134.1$ ($J=10.2$ Hz), 133.9 ($J=15.1$ Hz), 132.7 ($J=164.9$ Hz), 131.4 ($J=180.0$ Hz), 131.1 ($J=10.7$ Hz), 128.0 ($J=15.7$ Hz), 125.8 ($J=3.7$ Hz), 62.6 ($J=4.3$ Hz), 16.3 ppm ($J=5.7$ Hz); HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{14}H_{14}BrO_2P$: 323.9915; found: 323.9919.

**Phosphoryl triphenyl (8j)**: White solid, yield 71% (395 mg), m.p. 119–123 °C. $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=23.66$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=7.34$–$7.35$ (m, 6H), 7.18 (d, $J=7.56$ Hz, 6H), 7.00–7.05 ppm (m, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=132.8$ ($J=181.4$ Hz), 132.4 ($J=11.3$ Hz), 131.1 ($J=4.5$ Hz), 128.4 ppm ($J=16.5$ Hz); HR-EI-MS: $[M]^+$ $m/z$ calcd for $C_{18}H_{15}OP$: 278.0861; found: 278.0867.

**Phenylphosphinic acid (8k)**:[59] Oil, yield 74% (210 mg). $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=21.52$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=11.28$ (br s, 1H), 7.75–7.80 (m, 2H), 7.59 (d, $J=7.56$ Hz, 2H), 7.44–7.45 (m, 1H), 6.16 ppm (d, $J=566$ Hz); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=133.0$ ($J=3.7$ Hz), 132.0 ($J=3.6$ Hz), 129.7 ($J=185.7$ Hz), 128.4 ppm ($J=13.6$ Hz); HR-ESI-MS: $[M+H]^+$ $m/z$ calcd for $C_6H_8O_2P$: 143.0262; found: 143.0256.

**Diphenylphosphinic acid (8l)**:[60] White solid, yield 41% (268 mg), m.p. 129–134 °C. $^{31}$P NMR ($CDCl_3$, 121 MHz): $\delta=25.81$. $^1$H NMR ($CDCl_3$, 300 MHz): $\delta=9.71$ (br s, 1H), 7.64–7.67 (m, 4H), 7.48 (d, $J=7.56$ Hz, 4H), 7.30–7.34 ppm (m, 2H); $^{13}$C NMR ($CDCl_3$, 75 MHz): $\delta=134.1$ ($J=10.1$ Hz), 131.2 ($J=147.1$ Hz), 131.1 ($J=15.1$ Hz), 128.3 ppm ($J=4.3$ Hz); HR-ESI-MS: $[M+H]^+$ $m/z$ calcd for $C_{12}H_{12}O_2P$: 219.0575; found: 219.0571.

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