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# An efficient heterogeneous cross-coupling of aryl iodides with diphenylphosphine catalyzed by copper (I) immobilized in MCM-41

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National Natural Science Foundation of China, Grant/Award Number: 21272044; Project of Innovation for Enhancing Guangdong Pharmaceutical University; Provincial Experimental Teaching Demonstration Center of Chemistry and Chemical Engineering The heterogeneous cross-coupling reaction of aryl iodides with diphenylphosphine was achieved in toluene at 115 °C in the presence of 10 mol% of phenanthroline-functionalized MCM-41-supported copper (I) complex (Phen-MCM-41-CuI) with  $Cs_2CO_3$  as base, yielding various unsymmetric triarylphosphines in good to excellent yields. This protocol can tolerate a wide range of functional groups and does not need the use of expensive additives or harsh reaction conditions. This heterogeneous Cu (I) catalyst exhibited the same catalytic activity as homogeneous CuI/Phen system, and could easily be recovered by a simple filtration of the reaction solution and recycled up to seven times without significant loss of activity.

## KEYWORDS

cross-coupling, heterogeneous catalysis, phenanthroline copper complex, supported copper catalyst, triarylphosphine

# **1** | INTRODUCTION

Tertiary arylphosphines as some of the most useful ligands have widely been applied in transition-metal-catalyzed reactions.<sup>[1]</sup> In addition, triarylphosphines are used as catalysts<sup>[2]</sup> and fundamental building blocks<sup>[3]</sup> in organic synthesis. The classical routes to arylphosphines involve reactions of phosphine halides with aryl Grignard or aryl lithium reagents, and are therefore incompatible with a wide range of functional groups.<sup>[1]</sup> Among various approaches for the preparation of arylphosphine ligands, direct C— P bond formation via transition-metal-catalyzed coupling of aryl halides/triflates with unprotected secondary phosphines has been shown to be one of the most valuable and highly efficient methods because this onepot route does not require introduction of protecting groups at phosphorus and is tolerant of a wide variety of functional groups. Since the first palladium-catalyzed C— P coupling of aryl halides with diarylphosphines was reported by Stelzer and co-workers,<sup>[4]</sup> the development of palladium-catalyzed,<sup>[5]</sup> copper-catalyzed<sup>[6]</sup> and nickelcatalyzed<sup>[7]</sup> phosphinations of aryl halides or aryl triflates for construction of tertiary phosphines has attracted considerable interest. Recently, catalytic reduction of tertiary phosphine oxides has also proven to be an alternative route to tertiary phosphines.<sup>[8]</sup>

Despite significant progress made in homogeneous Pd-, Cu- and Ni-catalyzed construction of triarylphosphines, the use of expensive palladium complexes as well as difficult recovery and non-recyclability of the metal catalysts make these methods of limited synthetic utility from economic and environmental points of view. In addition, homogeneous metal catalysis might cause heavy metal contamination of the desired isolated product since triarylphosphines could coordinate with palladium, copper and nickel to form the corresponding complexes.<sup>[9]</sup> Recycling of homogeneous metal catalysts is a task of great importance economically and environmentally in both the chemical and pharmaceutical industries, especially when expensive and/or toxic heavy metal catalysts are utilized.<sup>[10]</sup> An attractive solution to these problems is the substitution of homogeneous metal catalysts with their heterogeneous counterparts.<sup>[11]</sup> In recent years, heterogeneous copper catalysts have been successfully applied in carbon-carbon,<sup>[12]</sup> carbon-oxygen,<sup>[13]</sup> carbonnitrogen,<sup>[14]</sup> carbon-sulfur<sup>[15]</sup> and carbon-selenium<sup>[16]</sup> bond formation reactions. However, to the best of our knowledge, no examples of heterogeneous coppercatalyzed C- P bond construction have been described until now.

Mesoporous MCM-41 materials have recently been shown to be powerful supports for homogeneous metal catalysts.<sup>[17]</sup> Some palladium,<sup>[18]</sup> rhodium,<sup>[19]</sup> molybdenum,<sup>[20]</sup> gold<sup>[21]</sup> and copper<sup>[22]</sup> complexes have been grafted on MCM-41 and the resulting MCM-41-supported metal complexes have been applied in organic synthesis as highly efficient and recyclable catalysts. In order to further expand our Cu (I)–MCM-41 chemistry toolbox,<sup>[12c,d,15c,d,16,22]</sup> herein we report the synthesis of phenanthroline-functionalized MCM-41-supported copper (I) complexes and their catalytic efficiency in the cross-coupling of aryl iodides with diphenylphosphine.

### 2 | RESULTS AND DISCUSSION

A series of phenanthroline-functionalized MCM-41-supported copper (I) complexes (Phen-MCM-41-CuX) were prepared according to the procedure shown in Scheme 1. First, MCM-41 was condensed with 1-(1,10phenanthrolin-5-yl)-3-(3-(triethoxysilyl)propyl)urea in toluene, followed by silvlation with Me<sub>3</sub>SiCl to generate phenanthroline-functionalized MCM-41 (Phenthe MCM-41). The latter was then reacted with CuX in acetone to afford a series of Phen-MCM-41-CuX complexes as light green powders.

Phen-MCM-41-CuI was characterized using powder X-ray diffraction (XRD), nitrogen adsorption–desorption measurements and energy-dispersive X-ray spectroscopy (EDS). Figure 1 shows XRD patterns of the parent MCM-41 and Phen-MCM-41-CuI. Compared with diffraction pattern of the parent MCM-41, the (100) reflection of Phen-MCM-41-CuI was observed with decreased intensity after grafting the copper complex, while the (110) and (200) reflections became weak and diffuse, which may be caused by contrast matching between the silicate framework and organic moieties located inside the channels of MCM-41. These results indicate that the ordered mesoporous structure of the parent MCM-41 remains intact through the grafting procedure.

The nitrogen adsorption-desorption isotherms and pore size distributions for MCM-41 and Phen-MCM-41-CuI are presented in Figures 2 and 3, respectively. As expected, the isotherms in Figure 2 have marked changes



Phen-MCM-41-CuCl (**A**), CuX = CuCl Phen-MCM-41-CuBr (**B**), CuX = CuBr Phen-MCM-41-CuI (**C**), CuX = CuI Phen-MCM-41-CuOTf (D), CuX = CuOTfPhen-MCM-41-CuCN (E), CuX = CuCN

**SCHEME 1** Preparation of Phen-MCM-41-CuX complexes



**FIGURE 1** XRD patterns of parent MCM-41 (1) and Phen-MCM-41-CuI (2)



FIGURE 2 Nitrogen adsorption-desorption isotherms of MCM-41 and Phen-MCM-41-CuI



FIGURE 3 Pore size distributions of MCM-41 and Phen-MCM-41-CuI

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before and after grafting because of the introduction of organic moieties into the channels of MCM-41, but both samples showed type IV isotherms. As shown in Figure 3, the pore volume and size of Phen-MCM-41-CuI reduced significantly compared with those of MCM-41, also indicating that the organic moieties were introduced into the inner channels, but the pores still retained a narrow distribution. After grafting of the phenanthroline–copper (I) complex onto MCM-41, the surface area and pore diameter decreased from 904 m<sup>2</sup> g<sup>-1</sup> and 2.7 nm to 567 m<sup>2</sup> g<sup>-1</sup> and 2.3 nm, respectively. The EDS analysis shows the elements present in the material. EDS analysis of fresh Phen-MCM-41-CuI complex shows the presence of Si, O, C, N, I and Cu elements (Figure 4).

In our initial screening experiments, the reaction of diphenylphosphine with 4-iodoanisole was investigated to optimize the reaction conditions, and the results are summarized in Table 1. First, the effect of various immobilized copper complexes on the model reaction was examined using Cs<sub>2</sub>CO<sub>3</sub> as base and toluene as solvent at 115 °C (Table 1, entries 1-5). Among several heterogeneous copper catalysts tested, we found that Phen-MCM-41-CuI (C) was the most efficient and gave the desired 2a in 86% yield (Table 1, entry 3), while other copper catalysts Phen-MCM-41-CuCl (A), Phen-MCM-41-CuBr (B), Phen-MCM-41-CuOTf (D) and Phen-MCM-41-CuCN (E) were substantially less effective and afforded lower yields (Table 1, entries 1, 2, 4 and 5). Our next studies focused on the effect of bases on the model reaction, with a significant base effect being observed (Table 1, entries 3, 6–12). It was found that  $K_2CO_3$  and  $K_3PO_4$  were also effective bases and gave good yields, whilst NaOMe, NaOBu-t, KOBu-t and NaOAc were less effective and n-Bu<sub>3</sub>N was ineffective. So Cs<sub>2</sub>CO<sub>3</sub> was the best choice. When diglyme, dimethylformamide (DMF) and dioxane were used as solvents instead of toluene, low yields were obtained (Table 1, entries 13-15). Lowering the reaction temperature to 105 or 95 °C resulted in a decreased yield (Table 1, entries 16 and 17). When a homogeneous CuI/ Phen system was used as the catalyst, the desired product 2a was also isolated in 87% yield (Table 1, entry 18), indicating that the catalytic activity of the Phen-MCM-41-CuI complex was comparable to that of CuI/Phen combination. Finally, the amount of the supported copper catalyst was screened, and 10 mol% loading of copper was found to be optimal. A lower yield was observed and a longer reaction time was required when the amount of the catalyst was decreased to 5 mol% (Table 1, entry 19). Increasing the amount of the copper catalyst could shorten the reaction time, but did not improve the yield of 2a significantly (Table 1, entry 20). Therefore, the optimal catalytic system involved the use of C (10 mol%),



FIGURE 4 EDS analysis of Phen-MCM-41-CuI complex



	1 OCH3 +	P H H Copper c: (10 mc base, solver H	atalyst ht, 115 °C	OCH <sub>3</sub>	
Entry	Copper catalyst	Base	Solvent	Time (h)	Yield (%) <sup>b</sup>
1	А	$Cs_2CO_3$	Toluene	24	56
2	В	$Cs_2CO_3$	Toluene	24	32
3	С	$Cs_2CO_3$	Toluene	24	86
4	D	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	24	40
5	Е	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	24	34
6	С	K <sub>2</sub> CO <sub>3</sub>	Toluene	24	81
7	С	K <sub>3</sub> PO <sub>4</sub>	Toluene	24	78
8	С	NaOMe	Toluene	24	59
9	С	NaOBu- <i>t</i>	Toluene	24	53
10	С	KOBu-t	Toluene	24	27
11	С	NaOAc	Toluene	24	41
12	С	<i>n</i> -Bu <sub>3</sub> N	Toluene	36	0
13	С	Cs <sub>2</sub> CO <sub>3</sub>	Diglyme	24	73
14	С	Cs <sub>2</sub> CO <sub>3</sub>	DMF	24	62
15	С	Cs <sub>2</sub> CO <sub>3</sub>	Dioxane	24	38
16 <sup>c</sup>	С	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	36	69
17 <sup>d</sup>	С	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	48	46
18	CuI/Phen	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	24	87
19 <sup>e</sup>	С	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	48	76
20 <sup>f</sup>	С	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	14	87

<sup>a</sup>Reaction was performed with 1a (1.0 mmol), Ph<sub>2</sub>PH (1.2 mmol), base (1.5 mmol) and copper catalyst (0.10 mmol) in solvent (3 ml) at 115 °C under argon.

<sup>b</sup>Isolated yield based on **1a**.

<sup>c</sup>Reaction at 105 °C.

 $^{\rm d}Reaction$  at 95 °C.

 $^{\rm e}5$  mol% Phen-MCM-41-CuI was used.

<sup>f</sup>20 mol% Phen-MCM-41-CuI was used.

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TABLE 2 Heterogeneous copper-catalyzed synthesis of unsymmetric triarylphosphines via C- P coupling of aryl iodides with Ph<sub>2</sub>PH<sup>a</sup>



<sup>a</sup>Reaction was performed with **1** (1.0 mmol), Ph<sub>2</sub>PH (1.2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.5 mmol) and Phen-MCM-41-CuI (10 mol%) in toluene (3 ml) at 115 °C under argon for 24 h. Isolated yields are given based on **1**.

 $Cs_2CO_3$  as base in toluene at 115 °C under argon for 24 h (Table 1, entry 3).

With the optimal reaction conditions established, we next examined the scope and limitations of this heterogeneous copper-catalyzed C- P coupling reaction. The results are summarized in Table 2. The C- P coupling reactions of electron-neutral, electron-rich and electrondeficient aryl iodides **1b-x** with Ph<sub>2</sub>PH proceeded smoothly under the optimized conditions to afford the corresponding unsymmetric triarylphosphines 2b-x in good to excellent yields. For example, reaction of iodobenzene **1b** with Ph<sub>2</sub>PH gave triphenylphosphine 2b in 90% yield. The electron-rich aryl iodides 1c-e showed a reactivity similar to that of 4-iodoanisole (1a) and afforded the desired products **2c–e** in 78–87% yields. 3,5-Dimethyliodobenzene (1f) and 4-iodobiphenyl (1 g)also proved to be good coupling partners and produced the expected triarylphosphines **2f** and **2 g** in good yields. For electron-deficient aryl iodides bearing either weak electron-withdrawing groups such as fluoro, bromo and chloro (1 h-j) or strong electron-withdrawing groups such as trifluoromethyl, acetyl, cyano, nitro and ester (1 k-p), the C-P coupling reactions also proceeded effectively to give the corresponding triarylphosphines 2 h-p

in 74–89% yields. 3-Chloro-4-methyliodobenzene (1q) also gave the desired 2q in 83% yield. These results indicate that the electronic nature of the substituents on the benzene ring has limited influence on the heterogeneous copper-catalyzed C- P coupling reaction. Base-sensitive functional groups such as methyl ketone (1 l) and esters (10, 1p) are tolerated by this method. In addition, sterically hindered o-substituted aryl iodides such as 2-iodotoluene (**1r**), 2-iodoanisole (1 s), 2chloroiodobenzene (1 t), 2-iodobiphenyl (1u), methyl 2-iodobenzoate (1v) and 2.4-difluoroiodobenzene (1w) could undergo the C-P coupling reaction effectively to furnish the desired coupling products 2r-w in 64-76% yields. Even if highly sterically hindered 2,4,6trimethyliodobenzene (1x) was used as substrate, the expected product 2x was also isolated in 65% yield. It is noteworthy that the bulky 1-iodonaphthalene 1y was successfully coupled to diphenylphosphine to give 2y in excellent yield. Heteroatoms turned out to be compatible with the employed reaction conditions, the reactions of 2-iodothiophene (1z), 2-iodopyridine (1a') and 2-fluoro-3iodopyridine (1b') with diphenylphosphine affording the corresponding products 2z-b'in good yields. Encouraged by these results, we also carried out the reaction 6 of 10 WILEY Organometallic Chemistry

of bromobenzene with diphenylphosphine under the same conditions; unfortunately, only a trace of the desired product **2b** was detected, so 4-bromoiodobenzene (**1j**) was selectively subjected to the coupling reaction to produce the desired product **2j** in high yield. Even if electron-deficient aryl bromides such as 4-nitrobromobenzene and 4-bromobenzonitrile were used as substrates, the yields of the desired products were very low (<10%). The present method provides a quite general and practical route for the synthesis of a wide variety of unsymmetric triarylphosphines having various functionalities.

To confirm that the high activity of Phen-MCM-41-CuI results from the copper sites on the channel walls and not from leached copper species, the heterogeneity of Phen-MCM-41-CuI was tested by hot filtration.<sup>[23]</sup> The reaction of 4-iodoanisole (**1a**) with Ph<sub>2</sub>PH was



**SCHEME 2** Plausible mechanism for heterogeneous Cucatalyzed C— P coupling reaction

carried out until an approximately 50% conversion of **1a**. Then Phen-MCM-41-CuI was removed by filtration of the reaction mixture at 115 °C and the filtrate was allowed to react further at 115 °C under argon. In this case, no increase in conversion of **1a** was observed, indicating that leached copper species from Phen-MCM-41-CuI (if any) are not responsible for the observed activity. We also determined the copper content in the filtrate using inductively coupled plasma atomic emission spectroscopy (ICP-AES), and no copper was detected in the solution. These results demonstrated that the catalyst was stable during the C— P coupling reaction and the observed catalysis was intrinsically heterogeneous.

A plausible mechanism for the heterogeneous copper (I)-catalyzed cross-coupling reaction of diphenylphosphine with aryl iodides (1) is illustrated in Scheme 2. Firstly, oxidative addition of Ar-I (1) to Phen-MCM-41-CuI gives an MCM-41-immobilized 1,10phenanthroline-ArCu (III)I<sub>2</sub> intermediate A.<sup>[24]</sup> The latter subsequently reacts with diphenylphosphine in the presence of Cs<sub>2</sub>CO<sub>3</sub> to afford an MCM-41-immobilized 1,10-phenanthroline–ArCu (III)I–PPh<sub>2</sub> intermediate **B**. Finally, reductive elimination of intermediate B produces the desired triarylphosphine 2 and regenerates the Phen-MCM-41-CuI complex to complete the catalytic cycle.

Under the optimized conditions, the stability and recyclability of Phen-MCM-41-CuI were evaluated in the reaction between 1-iodonaphthalene and diphenylphosphine. The results are summarized in Table 3. Filtration of the crude mixture followed by washing of the resulting solid with distilled water and acetone allowed the easy recovery of Phen-MCM-41-CuI. The recovered catalyst could be recycled up to seven times, and almost the same yield of 2y was observed. In addition, ICP-AES analysis was conducted on the recovered catalyst after eight consecutive runs. The copper content was found to be 0.73 mmol g<sup>-1</sup>, revealing almost the same copper content as for the fresh catalyst.

	$1_{\mathbf{Y}} + Ph_{\mathbf{P}}Ph_{\mathbf{H}} - \frac{Phen-MCM-41-Cul}{(10 mol\%)} + Ph_{\mathbf{P}}Ph_{\mathbf{C}_{\mathbf{S}_{2}}CO_{3}, \text{ toluene, } 115 °C, Ar} + Ph_{\mathbf{P}}Ph_{\mathbf{P}}Ph_{\mathbf{S}_{2}}$										
Entry	Catalyst cycle	Time (h)	Yield (%) <sup>b</sup>	Entry	Catalyst cycle	Time (h)	Yield (%) <sup>b</sup>				
1	1st (fresh)	24	92	5	5th	24	91				
2	2nd	24	91	6	6th	24	91				
3	3rd	24	92	7	7th	26	90				
4	4th	24	90	8	8th	28	89				

TABLE 3 Recycling of Phen-MCM-41-CuI<sup>a</sup>

<sup>a</sup>Reaction was performed with **1y** (5.0 mmol), Ph<sub>2</sub>PH (6.0 mmol), Cs<sub>2</sub>CO<sub>3</sub> (7.5 mmol) and Phen-MCM-41-CuI (0.50 mmol) in toluene (10 ml) at 115 °C under argon.

<sup>b</sup>Isolated yield based on **1y**.

# 3 | CONCLUSIONS

In summary, we have developed a novel, practical and environmentally friendly route to unsymmetric triarylphosphines through cross-coupling reactions of aryl iodides with diphenylphosphine using Phen-MCM-41-CuI as catalyst. This new heterogeneous copper catalyst could be prepared by a simple procedure from commercially available and inexpensive reagents and exhibited the same catalytic activity as the homogeneous CuI/Phen system. The reactions generated a variety of unsymmetric triarylphosphines in good to excellent yields and tolerated a wide range of functional groups, including base-sensitive groups. In addition, this methodology offers the competitiveness of recyclability of the copper catalyst without significant decreases in activity, and the copper catalyst can be recovered by simple filtration and recycled up to seven times, thus making this procedure economically and environmentally more acceptable.

# 4 | EXPERIMENTAL

All chemicals were of reagent grade and used as purchased, unless otherwise noted. The mesoporous material MCM-41<sup>[17b]</sup> 1-(1,10-phenanthrolin-5-yl)-3-(3and (triethoxysilyl)propyl)urea<sup>[25]</sup> were prepared according to literature procedures. All reactions were performed in dried solvent under an inert atmosphere of argon. The products were purified by flash chromatography on silica gel. A mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane was generally used as eluent. <sup>1</sup>H NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer with tetramethylsilane as an internal standard in CDCl<sub>3</sub> as solvent. <sup>13</sup>C NMR spectra (100 MHz) were recorded with a Bruker Avance 400 MHz spectrometer in CDCl<sub>3</sub> as solvent. <sup>31</sup>P NMR spectra (121 MHz) were recorded with a Bruker Avance 400 MHz spectrometer in CDCl<sub>3</sub> as solvent. Melting points are uncorrected. Copper content was determined with ICP-AES (Atomscan16, TJA Corporation). Powder XRD patterns were obtained with a Damx-rA (Rigaku). Nitrogen adsorption-desorption isotherms were obtained using a Belsorp-HP (Bel Japan Inc.) at 77 K. Prior to gas adsorption measurements, materials were degassed for 6 h at 423 K. EDS was performed using a microscope.

# 4.1 | Preparation of Phen-MCM-41

To a suspension of 1.12 g of MCM-41 in 100 ml of dry toluene was added a solution of 1.48 g of 1-(1,10phenanthrolin-5-yl)-3-(3-(triethoxysilyl)propyl)urea in 10 ml of dry toluene. The reaction mixture was stirred at reflux under argon for 24 h. Then the solid was filtered and washed with CHCl<sub>3</sub> (20 ml), and dried under vacuum at 150 °C for 6 h. The solid was then soaked in a solution of 4.5 g of Me<sub>3</sub>SiCl in 70 ml of dry toluene at 25 °C with stirring for 24 h. The product was filtered, washed with acetone (3 × 20 ml) and Et<sub>2</sub>O (3 × 20 ml), and dried under vacuum at 110 °C for 6 h to afford 1.54 g of hybrid material Phen-MCM-41. The nitrogen content was determined to be 3.67 mmol g<sup>-1</sup> using elemental analysis.

# 4.2 | Synthesis of Phen-MCM-41-CuI (C)

In a small Schlenk tube, 1.22 g of Phen-MCM-41 was mixed with 0.215 g (1.1 mmol) of CuI in 25 ml of dry acetone. The reaction mixture was stirred at 60 °C for 24 h under argon. The resulting product was filtered by suction, washed with distilled water and acetone, and dried at 80 °C under vacuum for 6 h to afford 1.32 g of a light green copper complex (Phen-MCM-41-CuI). The nitrogen and copper contents were determined to be 3.42 and 0.74 mmol  $g^{-1}$ , respectively.

Phen-MCM-41-CuCl (A), Phen-MCM-41-CuBr (B), Phen-MCM-41-CuOTf (D) and Phen-MCM-41-CuCN (E) were also prepared using Phen-MCM-41 (1.2 g) and 1.1 mmol of CuX (X = Cl, Br, OTf, CN) as the starting materials in the same manner. The copper contents were determined to be 0.73, 0.71, 0.70 and 0.66 mmol  $g^{-1}$ , respectively.

# 4.3 | General Procedure for Cross-Coupling of Diphenylphosphine with Various Aryl Iodides

Phen-MCM-41-CuI (135 mg, 0.1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.5 mmol) and aryl iodide 1 (1.0 mmol) (if solid) were placed in an oven-dried 20 ml Schlenk tube, and the reaction vessel was evacuated and filled with argon three times. Then 1 (1.0 mmol) (if liquid), diphenylphosphine (1.2 mmol) and toluene (3 ml) were added with a syringe under a counter flow of argon. The vessel was sealed with a screw cap, stirred at room temperature for 10 min and then connected to the Schlenk line filled with argon. The reaction mixture was stirred at 115 °C for 24 h. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with CH<sub>2</sub>Cl<sub>2</sub> (20 ml) and filtered. The Phen-MCM-41-CuI complex was washed with distilled water  $(2 \times 5 \text{ ml})$  and acetone  $(2 \times 5 \text{ ml})$ , and reused in the next run. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel to provide the product 2.

Diphenyl (4-methoxyphenyl) phosphine (**2a**).<sup>[6b]</sup> White solid; m.p. 67–68 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.25–7.16 (m, 12H), 6.82 (d, J = 8.0 Hz, 2H), 3.73 (s, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –7.10 (s).

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Triphenylphosphine (**2b**).<sup>[6b]</sup> White solid; m.p. 79– 80 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.44–7.23 (m, 15H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -5.45 (s).

Diphenyl (4-methylphenyl) phosphine (**2c**).<sup>[6b]</sup> White solid; m.p. 68–69 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ*, ppm): 7.37–7.14 (m, 14H), 2.34 (s, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, *δ*, ppm): -6.30 (s).

Diphenyl (3-methylphenyl) phosphine (**2d**).<sup>[26]</sup> White solid; m.p. 50–51 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ*, ppm): 7.42–7.06 (m, 14H), 2.30 (s, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, *δ*, ppm): –5.23 (s).

Diphenyl (4-aminophenyl) phosphine (**2e**).<sup>[4a]</sup> White solid; m.p. 37–38 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.23–7.12 (m, 10H), 7.06 (t, J = 7.6 Hz, 2H), 6.54 (d, J = 7.6 Hz, 2H), 3.43 (br, 2H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -6.61 (s).

Diphenyl (3,5-dimethylphenyl) phosphine (**2f**).<sup>[4a]</sup> Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.25– 7.12 (m, 10H), 6.89–6.83 (m, 3H), 2.16 (s, 6H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, δ, ppm): -5.28 (s).

4-(Diphenylphosphino) biphenyl (**2** g).<sup>[27]</sup> White solid; m.p. 83–84 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.58 (t, J = 8.0 Hz, 4H), 7.45–7.32 (m, 15H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -5.99 (s).

Diphenyl (4-fluorophenyl) phosphine (**2 h**).<sup>[28]</sup> White solid; m.p. 53–54 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.35–7.24 (m, 12H), 7.03 (t, J = 8.6 Hz, 2H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –6.58 (d).

Diphenyl (4-chlorophenyl) phosphine (**2i**).<sup>[29]</sup> White solid; m.p. 44–45 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.31–7.20 (m, 12H), 7.14 (t, J = 7.4 Hz, 2H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –6.48 (s).

Diphenyl (4-bomophenyl) phosphine (**2j**).<sup>[29]</sup> White solid; m.p. 78–79 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.45 (d, J = 7.6 Hz, 2H), 7.35–7.24 (m, 10H), 7.15 (t, J = 7.6 Hz, 2H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -6.44 (s).

Diphenyl (3-trifluoromethylphenyl) phosphine (**2** k).<sup>[30]</sup> Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.60–7.56 (m, 2H), 7.44–7.41 (m, 2H), 7.37–7.28 (m, 10H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –5.30 (s).

Diphenyl (4-acetylphenyl) phosphine (**2** 1).<sup>[6b]</sup> White solid; m.p. 121–122 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.80 (d, J = 7.2 Hz, 2H), 7.35–7.15 (m, 12H), 2.50 (s, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –5.07 (s).

Diphenyl (4-cyanophenyl) phosphine (**2** m).<sup>[31]</sup> White solid; m.p. 86–87 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.55 (dd, J = 8.4, 1.6 Hz, 2H), 7.38–7.29 (m, 12H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -4.46 (s).

Diphenyl (4-nitrophenyl) phosphine (**2n**).<sup>[32]</sup> Yellow solid; m.p. 134–135 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.14 (d, *J* = 7.6 Hz, 2H), 7.42–7.27 (m, 12H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –4.48 (s).

Methyl 4-(diphenylphosphino) benzoate (**20**).<sup>[6b]</sup> White solid; m.p. 103–104 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.97 (d, J = 7.2 Hz, 2H), 7.41–7.28 (m, 12H), 3.91 (s, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –5.05 (s).

Ethyl 4-(diphenylphosphino) benzoate (**2p**).<sup>[30]</sup> White solid; m.p. 83–84 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.98 (d, J = 8.4 Hz, 2H), 7.42–7.24 (m, 12H), 4.36 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -5.07 (s).

Diphenyl (3-chloro-4-methylphenyl) phosphine (**2q**). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.35– 7.24 (m, 11H), 7.19 (d, J = 7.6 Hz, 1H), 7.11–7.06 (m, 1H), 2.36 (s, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -5.96 (s). Anal. Calcd for C<sub>19</sub>H<sub>16</sub>ClP (%): C, 73.43; H, 5.19. Found (%): C, 73.17; H, 4.91.

Diphenyl (2-methylphenyl) phosphine (**2r**).<sup>[6b]</sup> White solid; m.p. 65–66 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.35–7.21 (m, 12H), 7.15–7.04 (m, 1H), 6.79–6.73 (m, 1H), 2.39 (s, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –13.27 (s).

Diphenyl (2-methoxyphenyl) phosphine (**2** s).<sup>[6b]</sup> White solid; m.p. 122–123 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.45–7.27 (m, 11H), 6.91–6.85 (m, 2H), 6.73–6.68 (m, 1H), 3.75 (s, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –16.61 (s).

Diphenyl (2-chlorophenyl) phosphine (**2** t).<sup>[33]</sup> White solid; m.p. 103–104 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.34–7.15 (m, 12H), 7.06 (t, J = 7.4 Hz, 1H), 6.69–6.65 (m, 1H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –10.87 (s).

2-(Diphenylphosphino) biphenyl (**2u**).<sup>[34]</sup> White solid; m.p. 60–61 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.33– 7.09 (m, 18H), 7.00–6.96 (m, 1H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –13.33 (s).

Methyl 2-(diphenylphosphino) benzoate (2v).<sup>[29]</sup> White solid; m.p. 97–98 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.05 (d, J = 2.8 Hz, 1H), 7.38–7.23 (m, 12H), 6.94 (m, 1H), 3.73 (s, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): -4.26 (s).

Diphenyl (2,4-difluorophenyl) phosphine (**2w**). Pale yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.37-7.26 (m, 10H), 6.85–6.75 (m, 3H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –99.40 (m). Anal. Calcd for C<sub>18</sub>H<sub>13</sub>F<sub>2</sub>P (%): C, 72.48; H, 4.39. Found (%): C, 72.26; H, 4.15.

Diphenyl (2,4,6-trimethylphenyl) phosphine (**2x**). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.27–7.22 (m, 4H), 7.20–7.11 (m, 6H), 6.81 (s, 2H), 2.19 (s, 3H), 2.09 (s, 6H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –16.52 (s). Anal. Calcd for C<sub>21</sub>H<sub>21</sub>P (%): C, 82.87; H, 6.95. Found (%): C, 82.59; H, 6.81.

1-(Diphenylphosphino) naphthalene (**2y**).<sup>[6b]</sup> White solid; m.p. 122–123 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, *δ*, ppm): 7.87–7.82 (m, 2H), 7.49–7.23 (m, 15H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, *δ*, ppm): –14.13 (s).

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2-(Diphenylphosphino) thiophene (**2z**).<sup>[6b]</sup> White solid; m.p. 44–45 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.58 (d, J = 3.2 Hz, 1H), 7.48–7.06 (m, 12H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –19.99 (s).

2-(Diphenylphosphino) pyridine (**2a**').<sup>[35]</sup> White solid; m.p. 82–83 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.72 (d, *J* = 3.6 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.40–7.25 (m, 10H), 7.18 (t, *J* = 5.8 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –4.06 (s).

3-(Diphenylphosphino)-2-fluoropyridine (**2b'**). White solid; m.p. 61–63 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 8.18 (dd, J = 4.6, 1.0 Hz, 1H), 7.40–7.25 (m, 10H), 7.23–7.18 (m, 1H), 7.11–7.07 (m, 1H). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): –58.33 (d). Anal. Calcd for C<sub>17</sub>H<sub>13</sub>FNP (%): C, 72.59; H, 4.66; N, 4.98. Found (%): C, 72.33; H, 4.51; N, 4.75. Copies of <sup>1</sup>H NMR and <sup>31</sup>P NMR spectra of compounds 2a-2b' have been provided in Supporting Information section.

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