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Highly efficient heterogeneous copper-catalyzed decarboxylative cross-coupling of potassium polyfluorobenzoates with aryl halides leading to polyfluorobiaryls†

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The heterogeneous decarboxylative cross-coupling reaction of potassium polyfluorobenzoates with aryl iodides and bromides was achieved in diglyme or DMAc at 130 or 160 °C in the presence of 10–20 mol% of a 1,10-phenanthroline-functionalized MCM-41-immobilized copper(I) complex, [MCM-41-Phen-CuI], yielding a variety of polyfluorobiaryls in good to excellent yields. This heterogeneous copper(I) complex could easily be prepared via a simple procedure from commercially readily available and inexpensive reagents, exhibited the same catalytic activity as the homogeneous CuI/Phen system, and was recovered by filtration of the reaction solution and recycled at least 8 times without significant loss of catalytic activity.

1. Introduction

Polyfluorobiaryls are important molecules in the pharmaceutical chemistry[1] and materials science[2] and are often used as starting materials in organic synthesis.[3] Subsequently, a variety of methods have been developed to form polyfluorobiaryls. The traditional methods involve the palladium- or copper-catalyzed cross-coupling reactions of pre-functionalized polyfluoroarenes with aryl halides, which require the use of expensive organometallic starting materials such as boronic acids,[4] borate salts,[5] stannanes,[6] and copper species.[7] Besides these methods, the palladium- or copper-catalyzed C–H arylation of polyfluoroarenes with aryl halides,[8] arylboronic acids,[9] organosilicon reagents,[10] arenediazonium tetrafluoroborates,[11] and aryliodide(III) diacetates,[12] has provided an alternative approach to the synthesis of polyfluorobiaryls. Transition-metal-catalyzed decarboxylative cross-couplings using carboxylic acids as aryl sources are an attractive strategy for the construction of biaryl bonds because this method does not use expensive and sensitive organometallic reagents, and generates CO_2 instead of organometallic byproducts that are formed in Suzuki–Miyaura, Stille, Kumada, and Negishi reactions.[13] Furthermore, structurally diverse carboxylic acids are often inexpensive and commercially readily available. Recently, palladium-, nickel-

and copper-catalyzed decarboxylative cross-couplings of polyfluorobenzoic acids or polyfluorobenzoate salts with aryl halides[14] and palladium-catalyzed decarboxylative cross-coupling of aromatic carboxylic acids with polyfluoroarenes[15] have been reported to be highly efficient methods for the synthesis of polyfluorobiaryls.

Although significant progress has been achieved in construction of polyfluorobiaryls by homogeneous Pd-, Ni- and Cu-catalyzed decarboxylative cross-coupling reactions, the use of expensive palladium catalysts and about 10–20 mol% of nickel or copper catalysts has limited their applications in large-scale syntheses and industrial processes because homogeneous catalysis suffers from the problematic separation of the catalyst from the product for re-use.[16] Moreover, homogeneous catalysis might result in heavy metal contamination of the desired isolated product, which restricts the application of such systems in electronics and biomedicine. The heterogenization of the existing homogeneous transition-metal catalysts appears to be a logical solution to these problems.[17] There has been considerable interest in the development of heterogeneous catalytic systems that can be easily recycled whilst maintaining the inherent activity of the catalytic center. However, to the best of our knowledge, no examples of heterogeneous palladium-, nickel- and copper-catalyzed synthesis of polyfluorobiaryls have been reported until now.

Mesoporous MCM-41 materials have recently emerged as promising supports for immobilization because of their large and uniform pore sizes, ultrahigh surface areas, big pore volumes and rich silanol groups in the inner walls.[18] To date, some functionalized MCM-41-immobilized palladium,[19] rhodium,[20] molybdenum,[21] gold[22] and copper[23] complexes have

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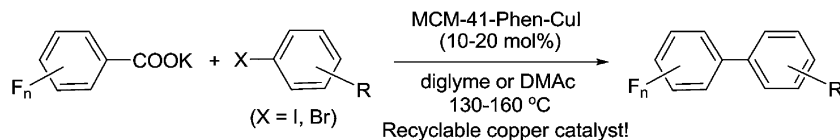
Scheme 1 Synthesis of polyfluorobiaryls *via* heterogeneous copper(I)-catalyzed decarboxylative cross-coupling of potassium polyfluorobenzoates with aryl halides.

been successfully used as potentially green and sustainable catalysts in organic reactions. Recently, we reported the first synthesis of MCM-41-immobilized 1,10-phenanthroline-copper(I) complex [MCM-41-Phen-CuI] and found that it is a highly efficient and recyclable heterogeneous catalyst for the C–O coupling reaction between aryl iodides and aliphatic alcohols.[24] In continuing our efforts to develop greener synthetic pathways for organic transformations,[19d–f,23,24] herein we wish to report a highly efficient, heterogeneous copper(I)-catalyzed decarboxylative cross-coupling of potassium polyfluorobenzoates with aryl halides leading to polyfluorobiaryls in good to excellent yields (Scheme 1).

2. Results and discussion

A series of MCM-41-immobilized 1,10-phenanthroline-copper(I) or (II) complexes [MCM-41-Phen-CuX$_n$] were easily prepared according to the procedure summarized in Scheme 2.[24] Firstly, the mesoporous MCM-41 (ref. 25) was condensed with 1-(1,10-phenanthrolin-5-yl)-3-(3-(triethoxysilyl)propyl)urea[26] in toluene under reflux for 24 h, followed by the silylation with Me$_3$SiCl in toluene at room temperature for 24 h to afford the 1,10-phenanthroline-functionalized MCM-41 [MCM-41-Phen]. The latter was then reacted with copper salts in acetone under reflux for 24 h to generate a series of MCM-41-immobilized 1,10-phenanthroline copper(I) or (II) complexes [MCM-41-Phen-CuX$_n$] as light green powders.

In our initial screening experiments, the reaction of C$_6$F$_5$COOK with PhI 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 by using DMAc as solvent at 130 °C (Table 1, entries 1–6). It is evident that lower yields were obtained when MCM-41-Phen-CuCl [**A**], MCM-41-Phen-CuBr [**B**], MCM-41-Phen-CuCl$_2$ [**D**], and MCM-41-Phen-CuBr$_2$ [**E**] were used as catalysts, and MCM-41-Phen-CuI [**C**] could give a moderate yield (entry 3), whilst MCM-41-Phen-Cu(OAc)$_2$ [**F**] afforded a low yield, so MCM-41-Phen-CuI [**C**] was finally selected as the catalyst for the reaction. Our next studies focused on the effect of solvent on the model reaction and a significant solvent effect was observed (Table 1, entries 3 and 7–10). When NMP, DMF and DMSO were used as solvents, low yields were obtained (entries 7, 9 and 10). To our delight, an excellent yield of 97% was achieved when diglyme was used as the solvent (entry 8). A possible explanation for this result is that diglyme can coordinate to potassium cation, which facilitates the reaction between the MCM-41-Phen-CuI complex and C$_6$F$_5$COO$^-$. The effect of temperature on the model reaction was also examined (Table 1, entries 8 and 11–13). For the temperatures tested [120, 130, 140 and 150 °C], 130 °C was the best choice (entry 8), and other temperatures were substantially less effective (entries 11–13). Finally, the amount of the immobilized 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 (entry 14). Increasing the amount of the copper catalyst could shorten the reaction time, but did not improve the yield of **3a** obviously (entry 15). When a homogeneous CuI/Phen was used as the catalyst, the desired product **3a** was also isolated in 98% yield (entry 16), which indicating that catalytic activity of MCM-41-Phen-CuI was comparable to that of
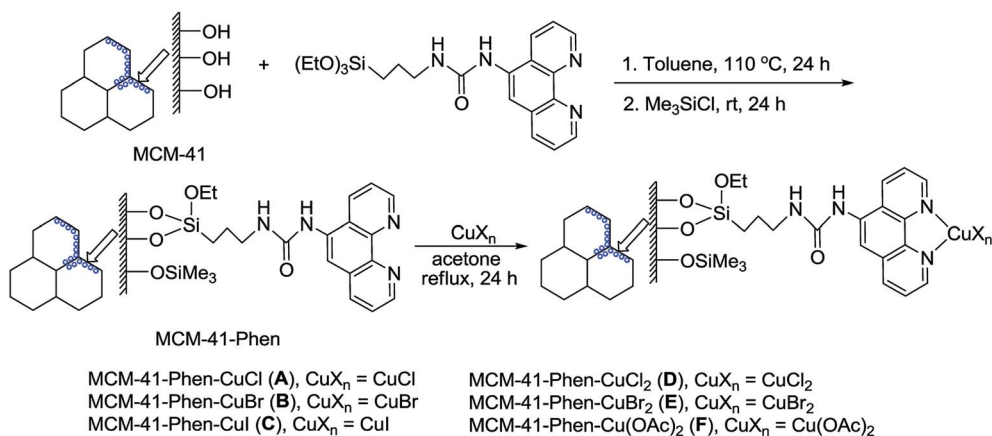
Scheme 2 Preparation of MCM-41-immobilized 1,10-phenanthroline copper(I) or (II) complexes.

Table 1 Screening of reaction conditions for the reaction of C_6F_5COOK with PhI^a
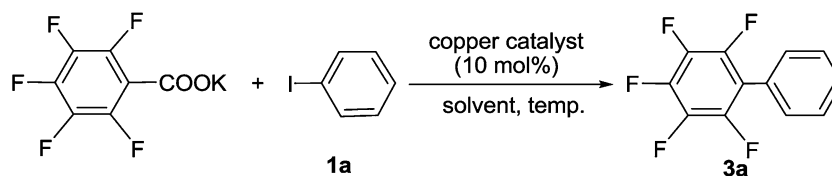
Entry	Copper catalyst	Solvent	Temp. (°C)	Time (h)	Yield^b (%)
1	**A**	DMAc	130	24	39
2	**B**	DMAc	130	24	44
3	**C**	DMAc	130	24	49
4	**D**	DMAc	130	24	38
5	**E**	DMAc	130	24	40
6	**F**	DMAc	130	24	18
7	**C**	NMP	130	24	41
8	**C**	Diglyme	130	24	97
9	**C**	DMF	130	24	37
10	**C**	DMSO	130	24	24
11	**C**	Diglyme	140	20	93
12	**C**	Diglyme	150	12	88
13	**C**	Diglyme	120	30	79
14^c	**C**	Diglyme	130	48	82
15^d	**C**	Diglyme	130	12	98
16	CuI/Phen	Diglyme	130	24	98
17^e	**C**	Diglyme	130	30	82

^{a} Reaction was performed with $C_6F_5CO_2K$ (0.75 mmol), **1a** (0.5 mmol) and copper catalyst (0.05 mmol) in solvent (0.5 mL) under Ar. ^{b} Isolated yield based on **1a**. ^{c} 5 mol% MCM-41-Phen-CuI was used. ^{d} 20 mol% MCM-41-Phen-CuI was used. ^{e} 1.0 equiv. of $C_6F_5CO_2K$ was used.

CuI/Phen combination. When 1.0 equiv. of C_6F_5COOK was used, the yield of **3a** was decreased to 82% (entry 17). Therefore, the optimal catalytic system involved the use of MCM-41-Phen-CuI [**C**] (10 mol%) and 1.5 equiv. of C_6F_5COOK in diglyme at 130 °C under Ar for 24 h (Table 1, entry 8).

With the optimal reaction conditions established, we tried to investigate the scope and limitations of this heterogeneous copper-catalyzed decarboxylative cross-coupling reaction and the results are summarized in Table 2. As shown in Table 2, both electron-deficient and electron-rich aryl iodides **1b–1j** underwent the decarboxylative cross-coupling reaction with C_6F_5COOK smoothly to afford the corresponding poly-fluorobiaryls **3b–3j** in 91–96% yields. The results indicated that the electronic natures of the substituents on benzene ring have limited influence on this heterogeneous copper-catalyzed decarboxylative cross-coupling reaction. The sterically congested electron-deficient aryl iodides such as 2-chlor-oiodobenzene **1k**, methyl 2-iodobenzoate **1l** and 2-nitroiodobenzene **1m** could also be successfully converted into the corresponding polyfluorobiaryls **3k–3m** in excellent yields. The electron-rich 2-iodotoluene **1n** and 2-iodoanisole **1o** showed slightly lower reactivity than the electron-deficient ortho-substituted iodobenzenes, however, the desired products **3n** and **3o** were also obtained in excellent yields by using 20 mol% of MCM-41-Phen-CuI as catalyst. A range of functional groups such as methyl, methoxy, chloro, fluoro, trifluoromethyl, nitro, cyano and ester were well tolerated. In addition to phenyl

iodides, heteroaryl iodides such as 3-, 2-, and 4-iodopyridines **1p–1r** and 3-iodothiophene **1s** also proved to be good coupling partners and gave the desired products **3p–3s** in high yields. Notably, bulky 1-iodonaphthalene **1t** could react with C_6F_5COOK effectively in the presence of 20 mol% of MCM-41-Phen-CuI to furnish the desired product **3t** in 96% yield.

Encouraged by the above results, we further investigated the scope and the generality of the method by varying aryl iodides to aryl bromides and the results are listed in Table 3. Generally, the reactivity of aryl bromides was lower than that of aryl iodides. Under the conditions optimized for aryl iodides, the reaction of bromobenzene with C_6F_5COOK gave the desired product **3a** in only 74% yield after 36 h. However, the yield of **3a** could be improved to 91% by increasing the amount of the catalyst to 20 mol%. As shown in Table 3, in the presence of 20 mol% of MCM-41-Phen-CuI, a variety of aryl bromides bearing either electron-withdrawing or electron-donating groups underwent decarboxylative cross-coupling reactions with C_6F_5COOK smoothly to give the corresponding poly-fluorobiaryls **3b–3d**, **3u**, **3f–3i** and **3v** in good to excellent yields. The electron-rich aryl bromides exhibited slightly lower reactivity than the electron-deficient ones and longer reaction times were required to complete the reactions. The ortho-substituted bromobenzenes such as 2-chlorobromobenzene and 2-bromotoluene also afforded the desired products **3k** and **3n** in excellent yields after 36 h. In addition to aryl bromides, heteroaryl bromides proved to be also suitable substrates and could
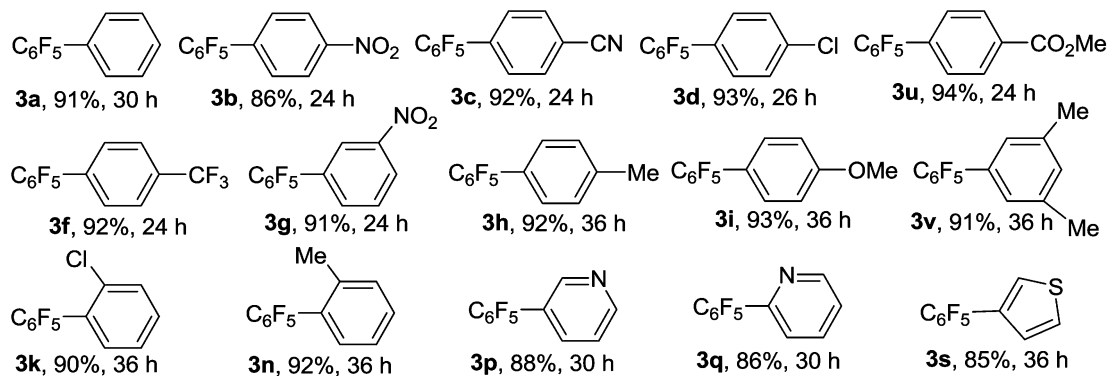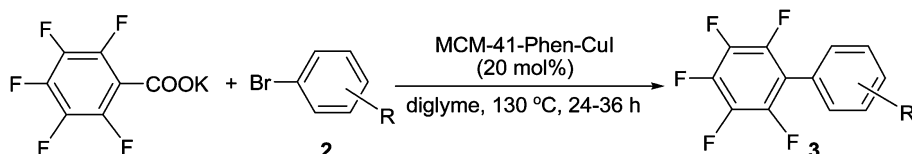
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Table 2 Heterogeneous copper-catalyzed decarboxylative cross-coupling between potassium pentafluorobenzoate and aryl iodides[a,b]
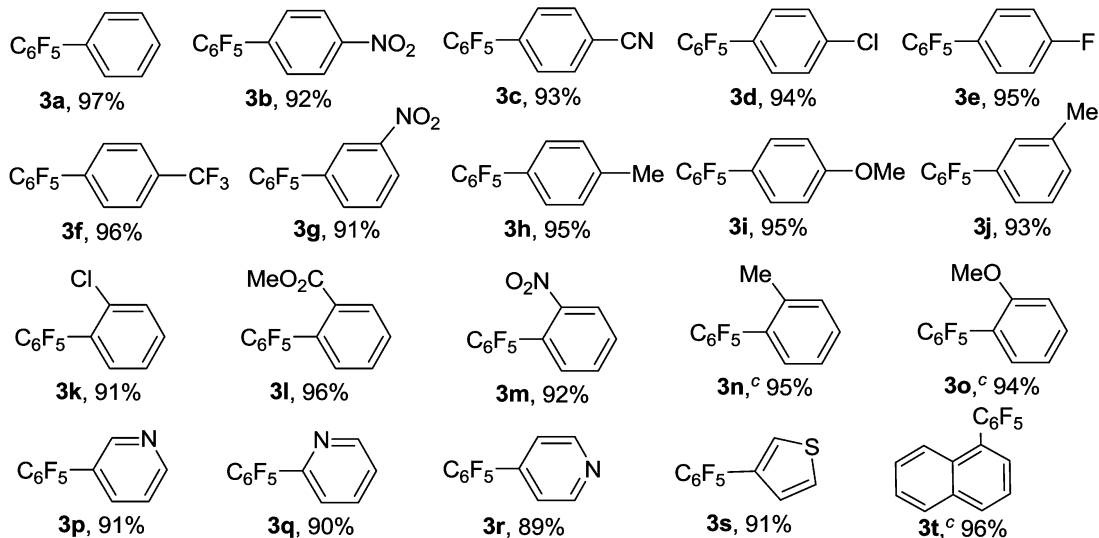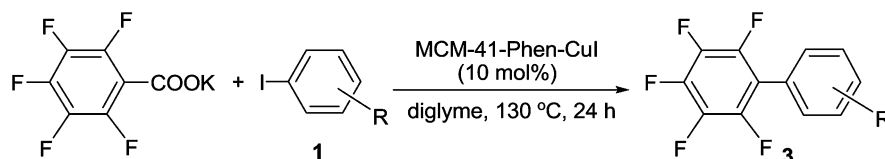
[a] Reaction was performed with potassium pentafluorobenzoate (0.75 mmol), **1** (0.5 mmol) and MCM-41-Phen-CuI (0.05 mmol) in diglyme (0.5 mL) at 130 °C under Ar for 24 h. [b] Isolated yield. [c] 20 mol% MCM-41-Phen-CuI was used.
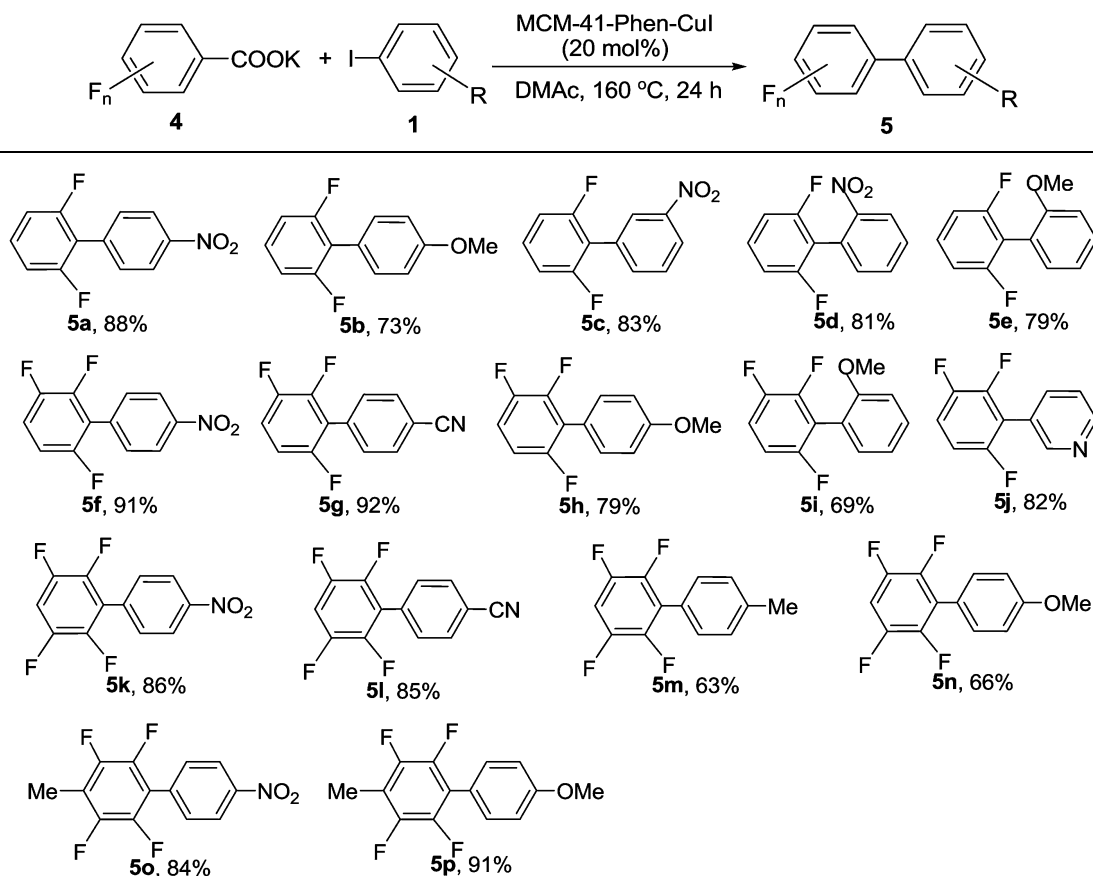
undergo the decarboxylative cross-coupling reaction effectively to give the corresponding polyfluorobiaryls **3p**, **3q** and **3s** in high yields.

The scope of the reaction with respect to fluoroarene was also examined and the results are presented in Table 4. Although diglyme plays an important role in the reactions with

Table 3 Heterogeneous copper-catalyzed decarboxylative cross-coupling between potassium pentafluorobenzoate and aryl bromides[a,b]

[a] Reaction was performed with potassium pentafluorobenzoate (0.75 mmol), **2** (0.5 mmol) and MCM-41-Phen-CuI (0.1 mmol) in diglyme (0.8 mL) at 130 °C under Ar for 24–36 h. [b] Isolated yield.

Table 4 Heterogeneous copper-catalyzed decarboxylative cross-coupling between aryl iodides and other polyfluorobenzoates[a,b]

5a, 88%   5b, 73%   5c, 83%   5d, 81%   5e, 79%

5f, 91%   5g, 92%   5h, 79%   5i, 69%   5j, 82%

5k, 86%   5l, 85%   5m, 63%   5n, 66%

5o, 84%   5p, 91%

[a] Reaction was performed with **4** (0.75 mmol), **1** (0.5 mmol) and MCM-41-Phen-CuI (0.1 mmol) in DMAc (0.8 mL) at 160 °C under Ar for 24 h.
[b] Isolated yield.

potassium pentafluorobenzoate, *N,N*-dimethyl acetamide (DMAc) can afford better results for fluoroarenes bearing fewer fluorine atoms. In addition, the use of 20 mol% of MCM-41-Phen-CuI and a high temperature of 160 °C were required due to their lower reactivity. Under the optimized reaction conditions, potassium monofluorobenzoate was found to be not suitable substrate and the reactions with aryl iodides generated traces of the desired products. This may be due to the fact that an *ortho*-F atom in potassium monofluorobenzoate can not activate the carboxylic group effectively. The decarboxylative cross-coupling reactions of potassium 2,6-difluorobenzoate **4a** with both electron-poor and electron-rich aryl iodides proceeded smoothly to afford the corresponding 2,6-difluorobiaryls **5a–5e** in good to high yields. The coupling reactions could tolerate strong electron-withdrawing or electron-donating groups and could also tolerate *ortho* substitution. In addition, tri- and tetrafluorobenzoates having two *ortho*-F atoms **4b**, **4c** and **4d** proved to be also good coupling partners and could undergo the decarboxylative cross-coupling reactions with a range of aryl iodides effectively to furnish the desired coupling products **5f–5p** in good to excellent yields. The method provides a quite general and practical route for the synthesis of

polyfluorobiaryls having various functionalities under green conditions.

To verify whether the observed catalysis was due to the heterogeneous catalyst MCM-41-1,10-Phen-CuI or to a leached copper species in solution, the reaction of C$_6$F$_5$COOK (1.5 mmol) with PhI (1.0 mmol) in diglyme (1.5 mL) was carried out until an approximately 50% conversion of PhI was reached. Then the MCM-41-1,10-Phen-CuI catalyst was removed from the reaction mixture by hot filtration[27] and the filtrate was allowed to react further by addition of C$_6$F$_5$COOK (0.8 mmol) at 130 °C under Ar atmosphere for 20 h. In this case, no significant increase in conversion of PhI was observed, indicating that leached copper species from the supported catalyst (if any) are not responsible for the observed activity. It was confirmed by ICP-AES analysis that no copper species could be detected in the filtrate (below the detection limit). These results rule out any contribution to the observed catalysis from a homogeneous copper species demonstrating that the catalyst was stable during the reaction and the observed catalysis was intrinsically heterogeneous.

A plausible mechanism for the heterogeneous copper(I)-catalyzed decarboxylative cross-coupling of potassium
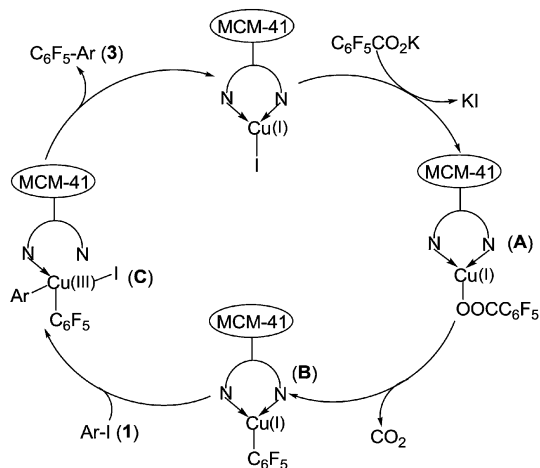
Scheme 3 Plausible mechanism for the heterogeneous Cu-catalyzed decarboxylative cross-coupling reaction.

polyfluorobenzoates with aryl halides is illustrated in Scheme 3. Firstly, the reaction of MCM-41-Phen-CuI with $C_6F_5CO_2K$ affords an MCM-41-immobilized 1,10-phenanthroline-Cu(I)–OCOC$_6$F$_5$ intermediate **A**, which then undergoes decarboxylation *via* a four-membered-ring transition state to form an MCM-41-immobilized 1,10-phenanthroline-Cu(I)–C$_6$F$_5$ intermediate **B**. The oxidative addition of Ar–I **1** to intermediate **B** gives an MCM-41-immobilized 1,10-phenanthroline-ArCu(III)I–C$_6$F$_5$ intermediate **C**. Finally, reductive elimination of intermediate **C** produces the desired product **3** and regenerates the MCM-41-Phen-CuI complex to complete the catalytic cycle.

For the practical application of a heterogeneous catalyst system its stability and recyclability are important factors. We next examined the reusability and stability of the MCM-41-Phen-CuI complex by using coupling reaction between iodobenzene (0.5 mmol) and $C_6F_5CO_2K$ (0.75 mmol) in diglyme (0.5 mL) in the presence of 10 mol% of MCM-41-Phen-CuI at 130 °C under argon atmosphere for 24 h. After carrying out the reaction, the catalyst was separated by simple filtration and washed with distilled water and EtOH. After being air-dried, it can be reused directly without further purification. The recovered
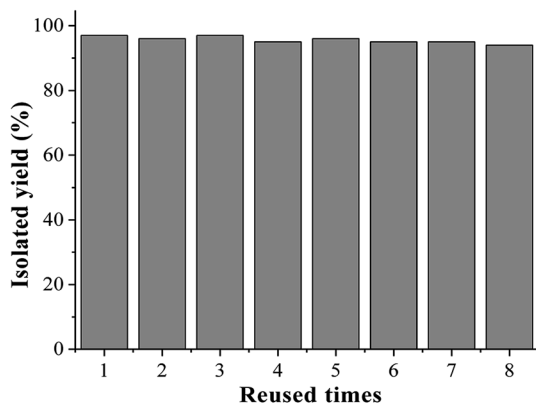
Fig. 1 Recycle of MCM-41-Phen-CuI complex.

catalyst was used in the next run, and almost the same yield of **3a** was obtained for 8 consecutive cycles (Fig. 1). In addition, copper leaching in the heterogeneous catalyst was also determined by ICP-AES analysis on the recovered catalyst after eight consecutive runs, which revealing almost the same copper content as the fresh one. In our opinion, the excellent catalytic activity and reusability of the copper catalyst relates to the efficient site isolation, to the optimal dispersion of the active sites on the inner channel walls and to the relatively strong interaction between the bidentate 1,10-phenanthroline ligand and the copper centre supported on the MCM-41. The result is important from the standpoint of green and sustainable chemistry.

3. Conclusions

In summary, we have successfully developed a novel, practical and environmentally friendly method for the synthesis of polyfluorobiaryls through the decarboxylative cross-coupling of readily accessible and nonvolatile potassium polyfluorobenzoates with aryl iodides or bromides by using an MCM-41-immobilized 1,10-phenanthroline-copper(I) complex [MCM-41-Phen-CuI] as catalyst. This heterogeneous copper catalyst could be easily 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 polyfluorobiaryls in good to excellent yields and were applicable to various polyfluorobenzoate salts and a wide range of aryl iodides or bromides. In addition, this methodology offers the competitiveness of recyclability of the copper catalyst without any decreases in activity, and the copper catalyst can be readily recovered by a simple filtration and reused at least 8 cycles, thus making this procedure economically and environmentally more acceptable.

4. Experimental

All chemicals were reagent grade and used as purchased. All solvents were dried and distilled before use. The MCM-41-Phen-CuCl [**A**], MCM-41-Phen-CuBr [**B**], MCM-41-Phen-CuI [**C**], MCM-41-Phen-CuCl$_2$ [**D**], MCM-41-Phen-CuBr$_2$ [**E**] and MCM-41-Phen-Cu(OAc)$_2$ [**F**] were prepared according to our previous procedure,[24] the copper contents were determined to be 0.73 mmol g^{-1}, 0.71 mmol g^{-1}, 0.74 mmol g^{-1}, 0.68 mmol g^{-1}, 0.70 mmol g^{-1} and 0.67 mmol g^{-1}, respectively. The products were purified by flash chromatography on silica gel. Mixture of EtOAc and hexane was generally used as eluent. ^{1}H NMR spectra were recoded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in CDCl$_3$ as solvent. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in CDCl$_3$ as solvent. ^{19}F NMR spectra (376 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in CDCl$_3$ as solvent with trifluorotoluene (TFT) ($\delta = -67.73$ ppm) as an external standard. Melting points are uncorrected. Copper content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation). HRMS spectra were

recorded on a Q-Tof spectrometer with micromass MS software using electrospray ionization (ESI).

4.1 General procedure for the decarboxylative cross-coupling of potassium pentafluorobenzoate with various aryl iodides

MCM-41-Phen-CuI (67 mg, 0.05 mmol), potassium penta-fluorobenzoate (188 mg, 0.75 mmol) and aryl iodide **1** (0.50 mmol) (if solid) were placed in an oven-dried 10 mL Schlenk tube, the reaction vessel was evacuated and filled with argon for three times. Then aryl iodide (0.50 mmol) (if liquid) and diglyme (0.5 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 130 °C for 24 h. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (20 mL) and filtered. The MCM-41-Phen-CuI complex was washed with distilled water (2 × 5 mL) and EtOH (2 × 5 mL), and reused in the next run. The organic layers were washed with water (2 × 20 mL), and then with brine, dried over $MgSO_4$, and filtered. The solvents were removed *via* rotary vapor and the residue was purified by flash column chromatography on silica gel to provide the product **3**.

4.2 General procedure for the decarboxylative cross-coupling of potassium pentafluorobenzoate with various aryl bromides

MCM-41-Phen-CuI (135 mg, 0.1 mmol), potassium penta-fluorobenzoate (188 mg, 0.75 mmol) and aryl bromide **2** (0.50 mmol) (if solid) were placed in an oven-dried 10 mL Schlenk tube, the reaction vessel was evacuated and filled with argon for three times. Then aryl bromide (0.50 mmol) (if liquid) and diglyme (0.8 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 130 °C for 24–36 h. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (20 mL) and filtered. The MCM-41-Phen-CuI complex was washed with distilled water (2 × 5 mL) and EtOH (2 × 5 mL), and reused in the next run. The organic layers were washed with water (2 × 20 mL), and then with brine, dried over $MgSO_4$, and filtered. The solvents were removed *via* rotary vapor and the residue was purified by flash column chromatography on silica gel to provide the product **3**.

4.3 General procedure for the decarboxylative cross-coupling of potassium perfluorobenzoates with various aryl iodides

MCM-41-Phen-CuI (135 mg, 0.1 mmol), potassium per-fluorobenzoate **4** (0.75 mmol) and aryl iodide **1** (0.50 mmol) (if solid) were placed in an oven-dried 10 mL Schlenk tube, the reaction vessel was evacuated and filled with argon for three times. Then aryl iodide (0.50 mmol) (if liquid) and DMAc (0.8 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 160 °C for

24 h. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (20 mL) and filtered. The MCM-41-Phen-CuI complex was washed with distilled water (2 × 5 mL) and EtOH (2 × 5 mL), and reused in the next run. The organic layers were washed with water (2 × 20 mL), and then with brine, dried over $MgSO_4$, and filtered. The solvents were removed *via* rotary vapor and the residue was purified by flash column chromatography on silica gel to provide the desired product **5**.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

References

1 (a) A. Zahn, C. Brotschi and C. J. Leumann, *Chem.–Eur. J.*, 2005, **11**, 2125–2129; (b) R. E. Mewshaw, R. J. Edsall Jr, C. Yang, E. S. Manas, Z. B. Xu, R. A. Henderson, J. C. Keith Jr and H. A. Harris, *J. Med. Chem.*, 2005, **48**, 3953–3979; (c) S. Purser, P. R. Moor, S. Swallow and V. Gouverneur, *Chem. Soc. Rev.*, 2008, **37**, 320–330; (d) M. de Candia, F. Liantonio, A. Carotti, R. De Cristofaro and C. Altomare, *J. Med. Chem.*, 2009, **52**, 1018–1028.

2 (a) J. R. Nitschke and T. D. Tilley, *J. Am. Chem. Soc.*, 2001, **123**, 10183–10190; (b) Y. Sakamoto, T. Suzuki, A. Miura, H. Fujikawa, S. Tokito and Y. Taga, *J. Am. Chem. Soc.*, 2000, **122**, 1832–1833; (c) V. A. Montes, G. Li, R. Pohl, J. Shinar and P. Anzenbacher, *Adv. Mater.*, 2004, **16**, 2001–2003; (d) P. Zacharias, M. C. Gather, M. Rojahn, O. Nuyken and K. Meerholz, *Angew. Chem., Int. Ed.*, 2007, **46**, 4388–4392.

3 (a) H. Amii and K. Uneyama, *Chem. Rev.*, 2009, **109**, 2119–2183; (b) S. M. Senaweera, A. Singh and J. D. Weaver, *J. Am. Chem. Soc.*, 2014, **136**, 3002–3005.

4 (a) T. Korenaga, T. Kosaki, R. Fukumura, T. Ema and T. Sakai, *Org. Lett.*, 2005, **7**, 4915–4917; (b) T. Kinzel, Y. Zhang and S. L. Buchwald, *J. Am. Chem. Soc.*, 2010, **132**, 14073–14075.

5 (a) H. J. Frohn, N. Y. Adonin, V. V. Bardin and V. F. Starichenko, *Tetrahedron Lett.*, 2002, **43**, 8111–8114; (b) H. J. Frohn, N. Y. Adonin, V. V. Bardin and V. F. Starichenko, *J. Fluorine Chem.*, 2002, **117**, 115–120.

6 P. L. Coe and G. M. Pearl, *J. Organomet. Chem.*, 1971, **31**, 55–57.

7 R. J. DePasquake and C. Tamborski, *J. Org. Chem.*, 1969, **34**, 1736–1740.

8 (a) M. Lafrance, C. N. Rowley, T. K. Woo and K. Fagnou, *J. Am. Chem. Soc.*, 2006, **128**, 8754–8756; (b) M. Lafrance, D. Shore and K. Fagnou, *Org. Lett.*, 2006, **8**, 5097–5100; (c)

H.-Q. Do and O. Daugulis, *J. Am. Chem. Soc.*, 2008, **130**, 1128–1129; (*d*) H.-Q. Do, R. M. Kashif and O. Daugulis, *J. Am. Chem. Soc.*, 2008, **130**, 15185–15192.

9 Y. Wei, J. Kan, M. Wang, W. Su and M. Hong, *Org. Lett.*, 2009, **11**, 3346–3349.

10 H. Fan, Y. Shang and W. Su, *Eur. J. Org. Chem.*, 2014, 3323–3327.

11 X. Zhu, F. Li and W. Su, *Tetrahedron Lett.*, 2013, **54**, 1285–1289.

12 Z. Fu, Q. Xiong, W. Zhang, Z. Li and H. Cai, *Tetrahedron Lett.*, 2015, **56**, 123–126.

13 (*a*) O. Baudoin, *Angew. Chem., Int. Ed.*, 2007, **46**, 1373–1375; (*b*) L. J. Goossen, N. Rodriguez and K. Goossen, *Angew. Chem., Int. Ed.*, 2008, **47**, 3100–3120; (*c*) L. J. Goossen, G. Deng and L. M. Levy, *Science*, 2006, **313**, 662–664; (*d*) D. Tanaka, S. P. Romeril and A. G. Myers, *J. Am. Chem. Soc.*, 2005, **127**, 10323–10333; (*e*) C. Wang, I. Piel and F. Glorius, *J. Am. Chem. Soc.*, 2009, **131**, 4194–4195; (*f*) J. D. Weaver, A. Recio, A. J. Grenning and J. A. Tunge, *Chem. Rev.*, 2011, **111**, 1846–1913; (*g*) W. L. Dzik, P. P. Lange and L. J. Goossen, *Chem. Sci.*, 2012, **3**, 2671–2678; (*h*) L. J. Goossen and K. Goossen, *Top. Organomet. Chem.*, 2013, **44**, 121–141.

14 (*a*) J.-M. Becht, C. Catala, C. Le Drian and A. Wagner, *Org. Lett.*, 2007, **9**, 1781–1784; (*b*) A. Voutchkova, A. Coplin, N. E. Leadbeater and R. H. Crabtree, *Chem. Commun.*, 2008, 6312–6314; (*c*) R. Shang, Y. Fu, Y. Wang, Q. Xu, H.-Z. Yu and L. Liu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9350–9354; (*d*) R. Shang, Q. Xu, Y.-Y. Jiang, Y. Wang and L. Liu, *Org. Lett.*, 2010, **12**, 1000–1003; (*e*) L. W. Sardzinski, W. C. Wertjes, A. M. Schnaith and D. Kalyani, *Org. Lett.*, 2015, **17**, 1256–1259.

15 H. Zhao, Y. Wei, J. Xu, J. Kan, W. Su and M. Hong, *J. Org. Chem.*, 2011, **76**, 882–893.

16 (*a*) C. E. Garrett and K. Prasad, *Adv. Synth. Catal.*, 2004, **346**, 889–900; (*b*) C. J. Welch, J. Albaneze-Walker, W. R. Leonard, M. Biba, J. DaSilva, D. Henderson, B. Laing, D. J. Mathre, S. Spencer, X. Bu and T. Wang, *Org. Process Res. Dev.*, 2005, **9**, 198–205; (*c*) S. Benyahya, F. Monnier, M. Wong Chi Man, C. Bied, F. Ouazzani and M. Taillefer, *Adv. Synth. Catal.*, 2008, **350**, 2205–2208; (*d*) S. Benyahya, F. Monnier, M. Wong Chi Man, C. Bied, F. Ouazzani and M. Taillefer, *Green Chem.*, 2009, **11**, 1121–1123; (*e*) P.-H. Li and L. Wang, *Adv. Synth. Catal.*, 2006, **348**, 681–685; (*f*) J. Yang, P. Li and L. Wang, *Tetrahedron*, 2011, **67**, 5543–5549; (*g*) P. Li, L. Wang, L. Zhang and G.-W. Wang, *Adv. Synth. Catal.*, 2012, **354**, 1307–1318; (*h*) L. Zhang, P. Li, C. Liu, J. Yang, M. Wang and L. Wang, *Catal. Sci. Technol.*, 2014, **4**, 1979–1988.

17 For selected reviews, see: (*a*) N. T. S. Phan, M. V. D. Sluys and C. W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609–679; (*b*) L. Yin and J. Liebscher, *Chem. Rev.*, 2007, **107**, 133–173; (*c*)

R. Akiyama and S. Kobayashi, *Chem. Rev.*, 2009, **109**, 594–642; (*d*) M. J. Climent, A. Corma and S. Iborra, *Chem. Rev.*, 2011, **111**, 1072–1133; (*e*) A. Molnar, *Chem. Rev.*, 2011, **111**, 2251–2320; (*f*) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2012, **112**, 1196–1231.

18 (*a*) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710–712; (*b*) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834–10843; (*c*) W. Zhou, J. M. Thomas, D. S. Shephard, B. F. G. Johnson, D. Ozkaya, T. Maschmeyer, R. G. Bell and Q. Ge, *Science*, 1998, **280**, 705–708.

19 For selected examples, see: (*a*) P. C. Mehnert, D. W. Weaver and J. Y. Ying, *J. Am. Chem. Soc.*, 1998, **120**, 12289–12296; (*b*) K. Mukhopadhyay, B. R. Sarkar and R. V. Chaudhari, *J. Am. Chem. Soc.*, 2002, **124**, 9692–9693; (*c*) J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem., Int. Ed.*, 1999, **38**, 56–77; (*d*) M. Cai, G. Zheng and G. Ding, *Green Chem.*, 2009, **11**, 1687–1693; (*e*) M. Cai, J. Peng, W. Hao and G. Ding, *Green Chem.*, 2011, **13**, 190–196; (*f*) W. Hao, H. Liu, L. Yin and M. Cai, *J. Org. Chem.*, 2016, **81**, 4244–4251; (*g*) F. Havasi, A. Ghorbani-Choghamarani and F. Nikpour, *New J. Chem.*, 2015, **39**, 6504–6512.

20 (*a*) S.-G. Shyu, S.-W. Cheng and D.-L. Tzou, *Chem. Commun.*, 1999, 2337–2338; (*b*) Y. Yang and R. M. Rioux, *Chem. Commun.*, 2011, **47**, 6557–6559.

21 (*a*) C. D. Nunes, A. A. Valente, M. Pillinger, A. C. Fernandes, C. C. Romao, J. Rocha and I. S. Goncalves, *J. Mater. Chem.*, 2002, **12**, 1735–1742; (*b*) M. Jia, A. Seifert and W. R. Thiel, *Chem. Mater.*, 2003, **15**, 2174–2180.

22 (*a*) A. Corma, E. Gutierrez-Puebla, M. Iglesias, A. Monge, S. Perez-Ferreras and F. Sanchez, *Adv. Synth. Catal.*, 2006, **348**, 1899–1907; (*b*) A. Corma, C. Gonzalez-Arellano, M. Iglesias and F. Sanchez, *Angew. Chem., Int. Ed.*, 2007, **46**, 7820–7822; (*c*) G. Villaverde, A. Corma, M. Iglesias and F. Sanchez, *ACS Catal.*, 2012, **2**, 399–406.

23 (*a*) R. Xiao, H. Zhao and M. Cai, *Tetrahedron*, 2013, **69**, 5444–5545; (*b*) H. Zhao, W. He, R. Yao and M. Cai, *Adv. Synth. Catal.*, 2014, **356**, 3092–3098; (*c*) M. Cai, R. Yao, L. Chen and H. Zhao, *J. Mol. Catal. A: Chem.*, 2014, **395**, 349–354; (*d*) H. Zhao, Y. Jiang, Q. Chen and M. Cai, *New J. Chem.*, 2015, **39**, 2106–2111; (*e*) H. Zhao, W. He, L. Wei and M. Cai, *Catal. Sci. Technol.*, 2016, **6**, 1488–1495.

24 Y. Lin, M. Cai, Z. Fang and H. Zhao, *RSC Adv.*, 2016, **6**, 85186–85193.

25 M. H. Lim and A. Stein, *Chem. Mater.*, 1999, **11**, 3285–3295.

26 M.-J. Li, Z. Chen, V. Wing-Wah Yam and Y. Zu, *ACS Nano*, 2008, **2**, 905–912.

27 H. E. B. Lempers and R. A. Sheldon, *J. Catal.*, 1998, **175**, 62–69.