Highly efficient heterogeneous copper-catalysed O-arylation of phenols by nitroarenes leading to diaryl ethers

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The heterogeneous O-arylation of phenols by nitroarenes was achieved in DMF at 100 °C by using an MCM-41-immobilised bidentate nitrogen copper(II) complex [MCM-41-2N-Cu(OAc)$_2$] as catalyst, yielding a variety of unsymmetrical diaryl ethers in good to excellent yields. This heterogeneous copper catalyst can be easily prepared by a simple procedure from commercially readily available and inexpensive reagents, recovered by filtration of the reaction solution and recycled at least seven times without significant loss of activity.

Keywords: copper, arylation, diaryl ether, supported catalyst, heterogeneous catalysis

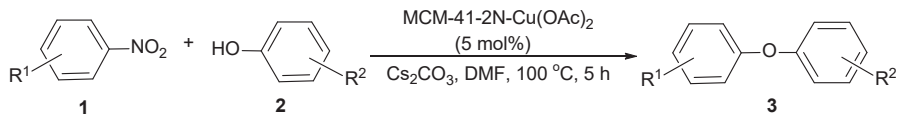
The diaryl ether linkage is present in a wide range of important compounds including a number of bioactive natural products,[1] non-natural useful agrochemicals[2] and natural or synthetic polymers.[3] Because of their relevance in life and material sciences, the development of methods for the synthesis of diaryl ethers is in high demand.[4] Classically, diaryl ethers are prepared by the Ullmann reaction of phenols with aryl halides promoted by stoichiometric or greater quantities of copper powder/salts at high temperatures in polar solvents,[5–7] but the harsh conditions seriously restrict this methodology. Recently, palladium[8–12]- and copper[13–17]-catalysed cross-coupling of aryl halides with phenols have been reported as improved methods for constructing diaryl ethers. Additionally, copper-catalysed Chan–Lam–Evans-type couplings of arylboronic acids with phenols[18-21] and couplings of nitroarenes with arylboronic acids[22] or phenols[23] are well-established methods for diaryl ether synthesis. Very recently, Itami and co-workers described palladium- or nickel-catalysed decarbonylative etherification of aromatic esters leading to diaryl ethers.[24]

Although these transition-metal-catalysed syntheses of diaryl ethers are highly efficient, in most cases homogeneous metal catalysts are used and the use of expensive palladium as well as the difficult recovery and non-recyclability of the metal catalysts make these methods of limited synthetic utility from environmental and economic points of view. In contrast, only a few heterogeneous versions have been reported, despite the practical benefits of heterogeneous catalysis. Often, catalysts for the Ullmann couplings of aryl halides with phenols have been grafted onto organic polymers [25] and carbon[26] as well as silica[27,28] or zeolite[29] materials. Whatever the performance of these heterogeneous materials, there is still a demand for alternative catalysts enabling Ullmann coupling reactions of high industrial relevance.

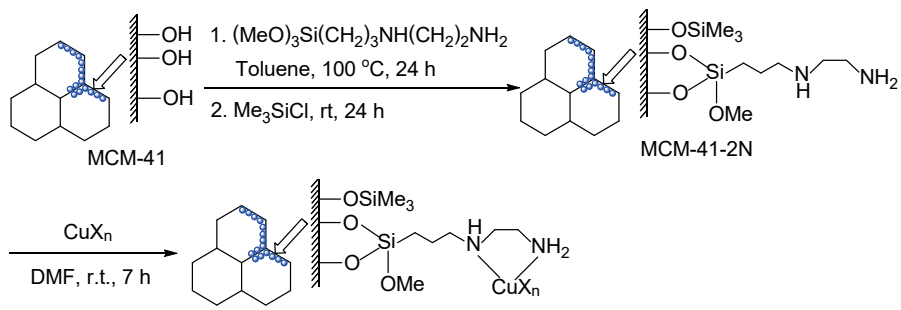
The discovery of the mesoporous material MCM-41 has provided a new possible candidate for an ideal heterogeneous support for immobilising homogeneous catalysts.[30] As we have recently shown, mesoporous MCM-41 materials are also powerful supports for copper species.[31–36] The MCM-41-supported bidentate nitrogen copper complexes proved to be highly efficient heterogeneous catalysts for the carbon–carbon[31,36] and carbon–heteroatom[32–35] bond formation reactions. In order further to expand our Cu-MCM-41 chemistry toolbox, here we report their catalytic efficiency in the O-arylation of phenols by nitroarenes (Scheme 1).

Results and discussion

A series of MCM-41-immobilised bidentate nitrogen copper(I) or copper(II) complexes (MCM-41-2N–CuX$_n$) was easily prepared starting from commercially available and inexpensive 3-(2-aminoethylamino)propyltrimethoxysilane and simple copper salts such as CuX$_n$ (X = Cl, Br, I, OAc, OTf) according to our previous procedure (Scheme 2).[31] Firstly, the mesoporous



Scheme 1



MCM-41-2N-CuCl [**A**], CuX$_n$ = CuCl
MCM-41-2N-CuI [**B**], CuX$_n$ = CuI
MCM-41-2N-CuCl$_2$ [**C**], CuX$_n$ = CuCl$_2$
MCM-41-2N-CuBr$_2$ [**D**], CuXn = CuBr$_2$
MCM-41-2N-Cu(OAc)$_2$ [**E**], CuX$_n$ = Cu(OAc)$_2$
MCM-41-2N-Cu(OTf)$_2$ [**F**], CuX$_n$ = Cu(OTf)$_2$

Scheme 2

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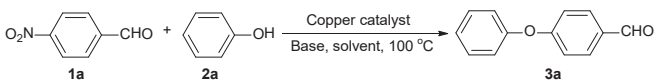
material MCM-41 was condensed with 3-(2-aminoethylamino) propyltrimethoxysilane in toluene at 100 °C for 24 h, followed by silylation with Me_3SiCl in dry toluene at room temperature for 24 h to afford 3-(2-aminoethylamino)propyl-functionalised MCM-41 (MCM-41-2N). The latter was subsequently reacted with various copper salts in DMF at room temperature for 7 h to generate a series of MCM-41-immobilised bidentate nitrogen copper(I) or copper(II) complexes (MCM-41-2N-CuX_n) as pale blue powders.

In our initial screening experiments, the reaction of 4-nitrobenzaldehyde (**1a**) with phenol (**2a**) was investigated to optimise the reaction conditions and the results are summarised in Table 1. First, the effect of various immobilised copper complexes on the model reaction was examined by using Cs_2CO_3 as base and DMF as solvent at 100 °C and a significant catalytic effect was observed (Table 1, entries 1–6). It is evident that good to excellent yields were obtained when MCM-41-2N-$CuCl_2$ [**C**], MCM-41-2N-$CuBr_2$ [**D**], MCM-41-2N-$Cu(OAc)_2$ [**E**] or MCM-41-2N-$Cu(OTf)_2$ [**F**] were used as the catalyst and that MCM-41-2N-$Cu(OAc)_2$ [**E**] gave an excellent result (Table 1, entry 5), whilst MCM-41-2N-CuCl [**A**] and MCM-41-2N-CuI [**B**] were substantially less efficient. MCM-41-2N-$Cu(OAc)_2$ [**E**] was therefore selected as the catalyst for the reaction. Our next studies focused on the effects of bases and solvents on the model reaction. For the bases tested (K_2CO_3, Cs_2CO_3, Na_2CO_3, $NaHCO_3$, $NaOBu^t$, $KOBu^t$, CsF and DABCO), K_2CO_3 and Na_2CO_3 afforded good yields and Cs_2CO_3 gave the best result, while other bases afforded low yields (Table 1, entries 5 and 7–13). When DMF was replaced by other solvents such as 1,4-dioxane, MeCN, xylene, toluene and pyridine, low yields were observed (Table 1, entries 14–18). Reducing the amount of the catalyst to 2.5 mol% resulted in a lower yield and a longer reaction time was required (Table 1, entry 19). Increasing the amount of the catalyst could shorten the reaction time, but did not improve the yield further (Table 1, entry 20). Therefore, the optimised catalytic system involved the use of MCM-41-2N-$Cu(OAc)_2$ [**E**] (5 mol%) and Cs_2CO_3 (2.0 equiv.) in DMF at 100 °C under Ar for 5 h (Table 1, entry 5).

With the optimised reaction conditions in hand, we tried to explore the scope of the heterogeneous copper-catalysed O-arylation of phenols by nitroarenes and the results are summarised in Table 2. As shown in Table 2, the reactions of 4-nitrobenzaldehyde (**1a**) with various phenols **2a–o** proceeded smoothly under the optimised conditions to give a variety of diaryl ethers **3a–o** in good to excellent yields (Table 2, entries 1–15). The electronic and steric effects of substituents on the phenyl ring of phenols have limited influence on the reaction. For example, the reactions of phenols bearing both electron-donating and weak electron-withdrawing groups **2b–g** gave the desired products **3b–g** in excellent yields (Table 2, entries 2–7), while phenols **2h** and **2i** having strong electron-withdrawing groups afforded a slightly lower yield of arylated products **3h** and **3i** (Table 2, entries 8 and 9). The sterically hindered *ortho*-substituted phenols **2j–m** also proved to be good substrates and furnished the corresponding diaryl ethers **3j–m** in good to excellent yields (Table 2. entries 10–13). In addition, the reactions of heterocyclic phenols such as pyridin-4-ol (**2n**)

Table 1 Optimisation of reaction conditions[a]



1a 2a 3a

Entry	Copper catalyst	Base	Solvent	Yield (%)[b]
1	MCM-41-2N-CuCl [**A**]	Cs_2CO_3	DMF	58
2	MCM-41-2N-CuI [**B**]	Cs_2CO_3	DMF	51
3	MCM-41-2N-$CuCl_2$ [**C**]	Cs_2CO_3	DMF	83
4	MCM-41-2N-$CuBr_2$ [**D**]	Cs_2CO_3	DMF	86
5	MCM-41-2N-$Cu(OAc)_2$ [**E**]	Cs_2CO_3	DMF	93
6	MCM-41-2N-$Cu(OTf)_2$ [**F**]	Cs_2CO_3	DMF	77
7	MCM-41-2N-$Cu(OAc)_2$ [**E**]	Na_2CO_3	DMF	75
8	MCM-41-2N-$Cu(OAc)_2$ [**E**]	K_2CO_3	DMF	82
9	MCM-41-2N-$Cu(OAc)_2$ [**E**]	$NaHCO_3$	DMF	44
10	MCM-41-2N-$Cu(OAc)_2$ [**E**]	CsF	DMF	42
11	MCM-41-2N-$Cu(OAc)_2$ [**E**]	$NaOBu^t$	DMF	54
12	MCM-41-2N-$Cu(OAc)_2$ [**E**]	$KOBu^t$	DMF	46
13	MCM-41-2N-$Cu(OAc)_2$ [**E**]	DABCO	DMF	25
14	MCM-41-2N-$Cu(OAc)_2$ [**E**]	Cs_2CO_3	Dioxane	14
15	MCM-41-2N-$Cu(OAc)_2$ [**E**]	Cs_2CO_3	MeCN	10
16	MCM-41-2N-$Cu(OAc)_2$ [**E**]	Cs_2CO_3	Xylene	12
17	MCM-41-2N-$Cu(OAc)_2$ [**E**]	Cs_2CO_3	Toluene	15
18	MCM-41-2N-$Cu(OAc)_2$ [**E**]	Cs_2CO_3	Pyridine	26
19[c]	MCM-41-2N-$Cu(OAc)_2$ [**E**]	Cs_2CO_3	DMF	78
20[d]	MCM-41-2N-$Cu(OAc)_2$ [**E**]	Cs_2CO_3	DMF	92

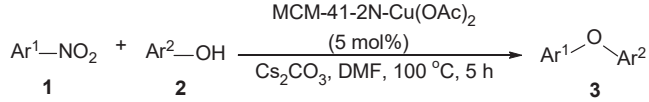
[a]All reactions were performed using **1a** (0.5 mmol), **2a** (1.0 mmol), copper catalyst (5 mol%), base (1.0 mmol), in solvent (3 mL) at 100 °C under Ar for 5 h.

[b]Isolated yield.

[c]Copper catalyst (2.5 mol%) was used for 12 h.

[d] Copper catalyst (10 mol%) was used for 3 h.

Table 2 Heterogeneous copper-catalysed O-arylation of phenols by nitroarenes[a]



1 2 3

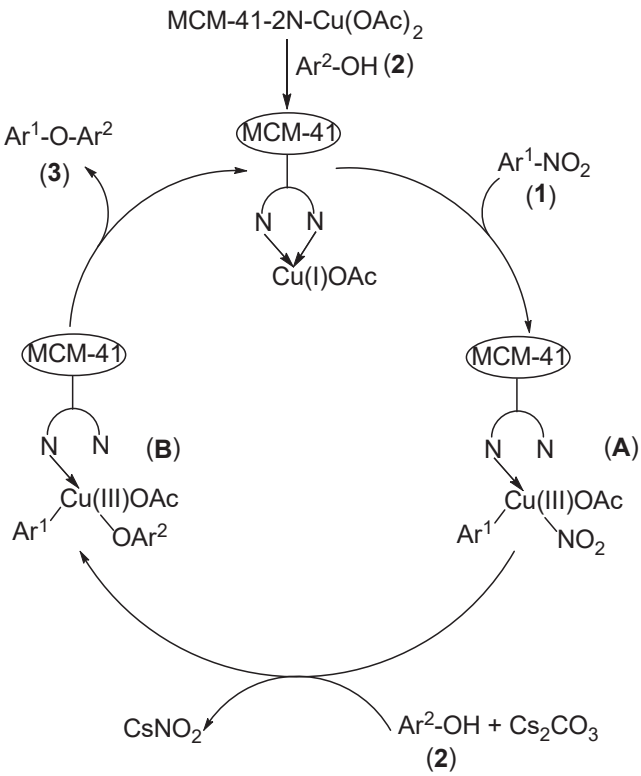
Entry	Ar^1	Ar^2	Product	Yield (%)[b]
1	4-$OHCC_6H_4$ (**1a**)	Ph (**2a**)	**3a**	93
2	4-$OHCC_6H_4$ (**1a**)	4-MeC_6H_4 (**2b**)	**3b**	93
3	4-$OHCC_6H_4$ (**1a**)	4-$MeOC_6H_4$ (**2c**)	**3c**	92
4	4-$OHCC_6H_4$ (**1a**)	3,5-$Me_2C_6H_3$ (**2d**)	**3d**	89
5	4-$OHCC_6H_4$ (**1a**)	4-ClC_6H_4 (**2e**)	**3e**	94
6	4-$OHCC_6H_4$ (**1a**)	4-BrC_6H_4 (**2f**)	**3f**	95
7	4-$OHCC_6H_4$ (**1a**)	4-FC_6H_4 (**2g**)	**3g**	95
8	4-$OHCC_6H_4$ (**1a**)	4-$CF_3C_6H_4$ (**2h**)	**3h**	69
9	4-$OHCC_6H_4$ (**1a**)	4-$CHOC_6H_4$ (**2i**)	**3i**	81
10	4-$OHCC_6H_4$ (**1a**)	2-BrC_6H_4 (**2j**)	**3j**	94
11	4-$OHCC_6H_4$ (**1a**)	2-MeC_6H_4 (**2k**)	**3k**	82
12	4-$OHCC_6H_4$ (**1a**)	2-PhC_6H_4 (**2l**)	**3l**	87
13	4-$OHCC_6H_4$ (**1a**)	2,6-$Me_2C_6H_3$ (**2m**)	**3m**	78
14	4-$OHCC_6H_4$ (**1a**)	4-Pyridinyl (**2n**)	**3n**	61
15	4-$OHCC_6H_4$ (**1a**)	2-(MeO_2C)-3-C_4H_2S (**2o**)	**3o**	67
16	2-$OHCC_6H_4$ (**1b**)	Ph (**2a**)	**3p**	96
17	2-$OHCC_6H_4$ (**1b**)	2-BrC_6H_4 (**2j**)	**3q**	85
18	4-NCC_6H_4 (**1c**)	Ph (**2a**)	**3r**	93
19	4-NCC_6H_4 (**1c**)	2-PhC_6H_4 (**2l**)	**3s**	79
20	4-NCC_6H_4 (**1c**)	4-$H_2NC_6H_4$ (**2p**)	**3t**	73
21	4-NCC_6H_4 (**1c**)	2-(MeO_2C)-3-C_4H_2S (**2o**)	**3u**	52
22	4-$MeOCOC_6H_4$ (**1d**)	Ph (**2a**)	**3v**	79
23	4-$MeOCOC_6H_4$ (**1d**)	4-$MeOC_6H_4$ (**2c**)	**3w**	72
24	4-$PhCOC_6H_4$ (**1e**)	Ph (**2a**)	**3x**	86
25	4-$PhCOC_6H_4$ (**1e**)	3,5-$Me_2C_6H_3$ (**2d**)	**3y**	82
26	4-$MeCOC_6H_4$ (**1f**)	Ph (**2a**)	**3z**	80
27	4-$F_3CC_6H_4$ (**1g**)	Ph (**2a**)	**3a′**	63
28	4-$O_2NC_6H_4$ (**1h**)	Ph (**2a**)	**3b′**	84
29	2-(Me)-4-C_5H_3N (**1i**)	Ph (**2a**)	**3c′**	81
30	2-(Me)-4-C_5H_3N (**1i**)	4-FC_6H_4 (**2g**)	**3d′**	62

[a]All reactions were performed using **1** (0.5 mmol), **2** (1.0 mmol), MCM-41-2N-$Cu(OAc)_2$ (5 mol%), Cs_2CO_3 (1.0 mmol), in DMF (3 mL) at 100 °C under Ar for 5 h.

[b]Isolated yield.

and methyl 3-hydroxythiophene-2-carboxylate (**2o**) proceeded effectively to afford the desired products **3n** and **3o** in good yields (Table 2, entries 14 and 15). We next examined the scope of nitroarenes by using various substituted nitrobenzenes as the substrates (Table 2, entries 16–28). Under the optimised conditions, not only a formyl substituent but also other electron-withdrawing groups such as cyano, methoxycarbonyl, benzoyl, acetyl, trifluoromethyl and nitro afforded the corresponding diaryl ethers **3r–b′** in moderate to high yields. The sterically congested 2-nitrobenzaldehyde (**1b**) showed as high reactivity as 4-nitrobenzaldehyde (**1a**) and the reactions with phenols gave the expected arylated products **3p** and **3q** in 96 and 85% yields respectively. Interestingly, when 1,4-dinitrobenzene was used as substrate, the mono-arylated product **3b′** was selectively formed in 84% yield (Table 2, entry 28). 2-Methyl-4-nitropyridine (**1i**) was also a suitable coupling partner and could react with phenol (**2a**) or 4-fluorophenol (**2g**) effectively to give the corresponding aryl heteroaryl ethers **3c′** and **3d′** in 81 and 62% yields respectively. It is noteworthy that the fluoro, chloro, and bromo moieties in phenols, which are often used for cross-coupling reactions, were all tolerated in our heterogeneous catalytic system (Table 2, entries 5–7, 10, 17 and 30), thereby making further elaborations of the corresponding diaryl ethers possible.

To verify whether the observed catalysis was due to the heterogeneous catalyst MCM-41-2N-Cu(OAc)$_2$ or to a leached copper species in solution, we performed the hot filtration test.[37] We focused on the O-arylation reaction of phenol (**2a**) by 4-nitrobenzaldehyde (**1a**). The MCM-41-2N-Cu(OAc)$_2$ complex was filtered off after 2 h of reaction and the filtrate allowed to react further. The catalyst filtration was performed at the reaction temperature (100 °C) in order to avoid possible recoordination or precipitation of soluble copper upon cooling. We found that, after this hot filtration, no further reaction was observed, indicating that leached copper species from the catalyst (if any) are not responsible for the observed activity.



Scheme 3

These results demonstrated that the heterogeneous MCM-41-2N-Cu(OAc)$_2$ was stable during the reaction and the O-arylation reaction catalysed by MCM-41-2N-Cu(OAc)$_2$ was intrinsically heterogeneous.

A plausible mechanism for this heterogeneous copper-catalysed O-arylation of phenols by nitroarenes is illustrated in Scheme 3. First, the MCM-41-2N-Cu(OAc)$_2$ complex is reduced to the MCM-41-2N-CuOAc complex by Ar^2–OH (**2**). Then oxidative addition of Ar^1–NO_2 (**1**) to the MCM-41-2N-CuOAc complex generates an MCM-41-anchored Ar^1–Cu(III)OAc–NO_2 intermediate (**A**). The latter reacts with Ar^2–OH (**2**) in the presence of Cs_2CO_3 to give an MCM-41-anchored Ar^1–Cu(III)OAc–OAr^2 intermediate (**B**). Finally, reductive elimination of intermediate (**B**) affords the desired Ar^1–O–Ar^2 (**3**) and regenerates the MCM-41-2N-CuOAc complex to complete the catalytic cycle.

For a heterogeneous transition metal catalyst system, it is important to evaluate the catalyst's ease of separation, recoverability and reusability. The MCM-41-2N-Cu(OAc)$_2$ can be easily recovered by simple filtration of the reaction solution. We next investigated the recyclability of the catalyst by using the O-arylation reaction of 4-bromophenol (**2f**) by 4-nitrobenzaldehyde (**1a**). After completion of the reaction, the catalyst was separated by simple filtration and washed with distilled water, DMF and ethanol. After being air-dried, it was reused directly without further purification in the next run and almost the same yield of the desired product **3f** was obtained for eight consecutive cycles (Fig. 1). The excellent recyclability of the catalyst should result from the chelating action of bidentate nitrogen ligand on copper and the mesoporous structure of the MCM-41 support. The result is important from industrial and environmental points of view.

In conclusion, we have successfully developed a novel, practical and environmentally-friendly method for the synthesis of unsymmetrical diaryl ethers through the O-arylation of phenols by nitroarenes by using an MCM-41-immobilised bidentate nitrogen copper(II) complex [MCM-41-2N-Cu(OAc)$_2$] as catalyst. The reactions generated a variety of unsymmetrical diaryl ethers in good to excellent yields and were applicable to a wide range of phenols and various nitroarenes. Importantly, this heterogeneous copper catalyst can be easily prepared from commercially available and inexpensive reagents, recovered by a simple filtration and recycled for at least seven cycles without significant loss of catalytic activity, thus making this procedure economically and environmentally more acceptable.

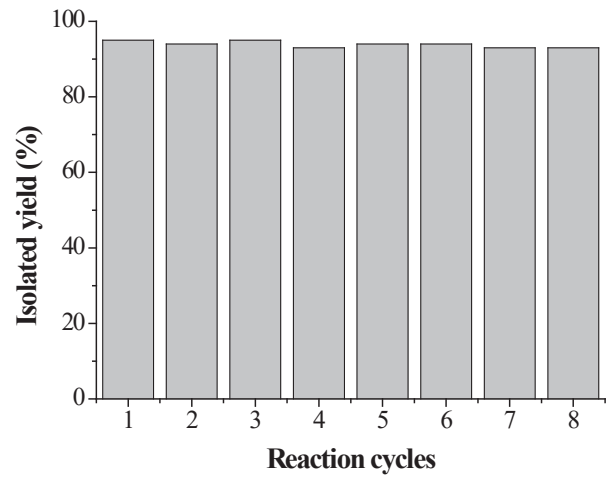


Fig. 1 Recycling of the MCM-41-2N-Cu(OAc)$_2$ catalyst.

Experimental

All reagents were used as received without further purification. The MCM-41-2N-CuCl [**A**], MCM-41-2N-CuI [**B**], MCM-41-2N-$CuCl_2$ [**C**], MCM-41-2N-$CuBr_2$ [**D**], MCM-41-2N-$Cu(OAc)_2$ [**E**] and MCM-41-2N-$Cu(OTf)_2$ [**F**] were prepared according to our previous procedure.[31] The copper contents were determined to be 0.48 mmol g^{-1}, 0.46 mmol g^{-1}, 0.51 mmol g^{-1}, 0.53 mmol g^{-1}, 0.55 mmol g^{-1} and 0.57 mmol g^{-1} respectively. All reactions were carried out under Ar in oven-dried glassware with magnetic stirring. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on a Bruker Avance 400 (100 MHz) spectrometer using $CDCl_3$ as the solvent. HRMS spectra were recorded on a quadrupole-time of flight Bruker MicroTOF-Q II mass spectrometer equipped with an ESI and APCI source. Copper content was determined with inductively coupled plasma atom emission spectroscopy using an Atomscan16 instrument (TJA Corporation).

Heterogeneous copper-catalysed O-arylation of phenols by nitroarenes; general procedure

Under an argon atmosphere, a Schlenk tube was charged with MCM-41-2N-$Cu(OAc)_2$ (46 mg, 0.025 mmol), nitroarene **1** (0.5 mmol), phenol **2** (1.0 mmol), Cs_2CO_3 (1.0 mmol) and DMF (3 mL). The reaction mixture was stirred at 100 °C for 5 h under Ar. After being cooled to room temperature, the mixture was diluted with ethyl acetate (20 mL) and filtered. The MCM-41-2N-$Cu(OAc)_2$ catalyst was washed with distilled water (2 × 5 mL), DMF (2 × 5 mL) and EtOH (2 × 5 mL) and could be reused in the next run. The filtrate was washed with water (2 × 10 mL) and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (EtOAc/hexane) on silica gel to afford the desired product **3**.

4-Phenoxybenzaldehyde (**3a**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.86–7.82 (m, 2H), 7.43–7.38 (m, 2H), 7.26–7.19 (m, 1H), 7.10–7.03 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 163.2, 155.1, 131.9, 131.3, 130.2, 124.9, 120.4, 117.6.

4-(4-Methylphenoxy)benzaldehyde (**3b**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 163.7, 152.7, 134.7, 131.9, 131.0, 130.7, 120.4, 117.2, 20.8.

4-(4-Methoxyphenoxy)benzaldehyde (**3c**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.06–6.99 (m, 4H), 6.96–6.91 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 164.1, 156.9, 148.2, 131.9, 130.9, 121.8, 116.8, 115.2, 55.7.

4-(3,5-Dimethylphenoxy)benzaldehyde (**3d**): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.86 (s, 1H), 6.70 (s, 2H), 2.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 163.5, 155.0, 140.1, 131.9, 131.1, 126.7, 118.1, 117.5, 21.3; HRMS calcd for $C_{15}H_{14}O_2^+$: [M^+]: 226.0994; found: 226.0986.

4-(4-Chlorophenoxy)benzaldehyde (**3e**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.07–7.01 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 162.7, 153.8, 132.0, 131.6, 130.2, 130.1, 121.7, 117.7.

4-(4-Bromophenoxy)benzaldehyde (**3f**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.93 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 162.6, 154.4, 133.2, 132.0, 131.7, 122.1, 117.8, 117.6.

4-(4-Fluorophenoxy)benzaldehyde (**3g**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.14–7.01 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 163.4, 159.7 (d, $^1J_{C-F}$ = 242.4 Hz), 150.8 (d, $^4J_{C-F}$ = 2.7 Hz), 132.0, 131.3, 122.5 (d, $^3J_{C-F}$ = 8.4 Hz), 117.2, 116.8 (d, $^2J_{C-F}$ = 23.3 Hz).

4-(4-Trifluoromethylphenoxy)benzaldehyde (**3h**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.18–7.12 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 161.7, 158.4, 132.3, 132.1, 127.5 (q, $^3J_{C-F}$ = 3.7 Hz), 126.7 (q, $^2J_{C-F}$ = 32.7 Hz), 123.9 (q, $^1J_{C-F}$ = 270.1 Hz), 119.8, 118.7.

4,4'-Oxydibenzaldehyde (**3i**): Pale yellow oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 4H), 7.19 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 161.0, 132.6, 132.1, 119.4.

4-(2-Bromophenoxy)benzaldehyde (**3j**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.19–7.02 (m, 2H), 7.00 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 162.4, 151.7, 134.2, 132.0, 129.1, 126.8, 122.7, 116.9, 116.2, 116.1.

4-(2-Methylphenoxy)benzaldehyde (**3k**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.31–7.15 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 163.4, 152.8, 132.1, 131.9, 131.0, 130.9, 127.6, 125.5, 121.1, 116.5, 16.0.

4-(Biphenyl-2-yloxy)benzaldehyde (**3l**): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.52–7.24 (m, 8H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 163.3, 151.6, 137.1, 134.8, 131.9, 131.6, 130.9, 129.1, 129.0, 128.3, 127.5, 125.8, 121.8, 117.0; HRMS calcd for $C_{19}H_{14}O_2^+$: [M^+]: 274.0994; found: 274.0989.

4-(2,6-Dimethylphenoxy)benzaldehyde (**3m**): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 7.83–7.79 (m, 2H), 7.15–7.07 (m, 3H), 6.90–6.85 (m, 2H), 2.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 162.9, 150.4, 132.3, 131.1, 130.7, 129.2, 125.8, 115.1, 16.2; HRMS calcd for $C_{15}H_{14}O_2^+$: [M^+]: 226.0994; found: 226.0995.

4-(Pyridin-4-yloxy)benzaldehyde (**3n**): Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.56 (d, *J* = 5.6 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 163.2, 159.6, 151.8, 133.2, 132.1, 120.3, 113.4; HRMS calcd for $C_{12}H_9NO_2^+$: [M^+]: 199.0633; found: 199.0625.

Methyl 3-(4-formylphenoxy)thiophene-2-carboxylate (**3o**): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.89–7.84 (m, 2H), 7.54 (t, *J* = 2.8 Hz, 1H), 7.12–7.08 (m, 2H), 6.84 (d, *J* = 5.6 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 162.7, 161.0, 155.0, 131.7, 131.6, 130.8, 122.5, 117.0, 99.6, 52.1; HRMS calcd for $C_{13}H_{10}O_4S^+$: [M^+]: 262.0300; found: 262.0295.

2-Phenoxybenzaldehyde (**3p**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.45 (s, 1H), 7.87 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.47–7.44 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.15–7.08 (m, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 160.0, 156.4, 135.8, 130.1, 128.5, 126.9, 124.3, 123.3, 119.4, 118.5.

2-(2-Bromophenoxy)benzaldehyde (**3q**): Colourless oil;[38] ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.52 (s, 1H), 7.89–7.86 (m, 1H), 7.61–7.58 (m, 1H), 7.44–7.38 (m, 1H), 7.29–6.97 (m, 4H), 6.66 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 159.5, 152.5, 135.8, 134.2, 129.0, 128.6, 126.3, 123.4, 121.7, 117.0, 116.4, 115.5.

4-Phenoxybenzonitrile (**3r**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 154.8, 134.2, 130.3, 125.2, 120.4, 118.9, 117.9, 105.8.

4-(Biphenyl-2-yloxy)benzonitrile (**3s**): Colourless oil;[39] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.24 (m, 10H), 7.11 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.87–6.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 151.3, 137.0, 134.8, 134.0, 131.7, 129.2, 129.0, 128.3, 127.6, 126.0, 121.8, 118.9, 117.3, 105.3.

4-(4-Aminophenoxy)benzonitrile (**3t**): Yellow oil;[40] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.53 (m, 2H), 6.96–6.92 (m, 2H), 6.89–6.85 (m, 2H), 6.73–6.69 (m, 2H), 3.71 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 146.3, 144.1, 134.0, 121.9, 119.1, 117.0, 116.3, 104.9.

Methyl 3-(4-cyanophenoxy)thiophene-2-carboxylate (**3u**): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.60 (m, 2H), 7.55 (d, *J* = 5.6 Hz, 1H), 7.06–7.02 (m, 2H), 6.83 (d, *J* = 5.6 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 160.9, 159.2, 134.2, 130.9, 122.5, 118.7, 118.1, 106.5, 97.8, 52.1; HRMS calcd for $C_{13}H_9NO_3S^+$: [M^+]: 259.0303; found: 259.0307.

Methyl 4-phenoxybenzoate (**3v**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 161.8, 155.7, 131.7, 130.0, 124.5, 124.4, 120.1, 117.3, 52.0.

Methyl 4-(4-methoxyphenoxy)benzoate (**3w**): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 4H), 3.89 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 162.8, 156.6, 148.6, 131.6, 123.9, 121.7, 116.3, 115.1, 55.7, 52.0; HRMS calcd for $C_{15}H_{14}O_4^+$: [M^+]: 258.0892; found: 258.0893.

4-Phenoxybenzophenone (**3x**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5, 161.7, 155.6, 138.0, 132.5, 132.2, 131.9, 130.1, 129.8, 128.3, 124.6, 120.2, 117.2.

4-(3,5-Dimethylphenoxy)benzophenone (**3y**): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.76 (m, 4H), 7.60–7.55 (m, 1H), 7.50–7.45 (m, 2H), 7.03–7.00 (m, 2H), 6.84 (s, 1H), 6.71 (s, 2H), 2.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.6, 161.9, 155.4, 140.0, 138.0, 132.5, 132.1, 131.7, 129.9, 128.3, 126.4, 117.9, 117.1, 21.3; HRMS calcd for $C_{21}H_{18}O_2^+$: [M^+]: 302.1307; found 302.1305.

4'-Phenoxyacetophenone (**3z**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.23–7.18 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.9, 162.0, 155.5, 131.8, 130.6, 130.1, 124.7, 120.2, 117.3, 26.5.

4-Trifluoromethyldiphenyl ether (**3a'**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.99–6.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 155.7, 130.1, 127.1 (q, $^3J_{C-F}$ = 3.7 Hz), 124.8 (q, $^2J_{C-F}$ = 32.7 Hz), 124.5, 124.2 (q, $^1J_{C-F}$ = 269.8 Hz), 119.9, 117.9.

4-Nitrodiphenyl ether (**3b'**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.17 (m, 2H), 7.47–7.41 (m, 2H), 7.28–7.24 (m, 1H), 7.11–7.02 (m, 2H), 7.00–6.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 154.7, 142.6, 130.4, 126.0, 125.5, 120.6, 117.1.

2-Methyl-4-phenoxypyridine (**3c'**): Colourless oil;[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 5.6 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 6.8 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.68 (s, 1H), 6.66 (d, *J* = 6.0 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 160.5, 154.3, 150.6, 130.1, 125.2, 120.8, 111.4, 109.6, 24.5.

4-(4-Fluorophenoxy)-2-methylpyridine (**3d'**): Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 5.6 Hz, 1H), 7.10 (t, *J* = 8.4 Hz, 2H), 7.06–7.02 (m, 2H), 6.65 (d, *J* = 2.4 Hz, 1H), 6.63–6.61 (m, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 160.6, 159.9 (d, $^1J_{C-F}$ = 242.7 Hz), 150.7, 149.9 (d, $^4J_{C-F}$ = 2.7 Hz), 122.3 (d, $^3J_{C-F}$ = 8.4 Hz), 116.8 (d, $^2J_{C-F}$ = 23.3 Hz), 111.0, 109.3, 24.5; HRMS calcd for $C_{12}H_{10}FNO^+$: [M^+]: 203.0746; found 203.0751.

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