MCM-41-immobilised nitrogen and sulfur mixed tridentate palladium(0) complex: a highly efficient and recyclable catalyst for the Suzuki reaction of aryl bromides in air

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The novel MCM-41-immobilised nitrogen and sulfur mixed tridentate palladium(0) complex [MCM-41-2N,S-Pd(0)] was prepared from 3-(2-aminoethylamino)propyltrimethoxysilane by immobilisation on MCM-41, followed by reaction with thiophene-2-carboxaldehyde and $PdCl_2$ and then reduction with hydrazine hydrate. This phosphine-free heterogeneous palladium(0) complex was a highly active catalyst for the Suzuki reaction of aryl bromides in air and could be recycled at least 8 times without significant loss of activity.

Keywords: palladium, Suzuki coupling, functionalised MCM-41, aryl bromide, heterogeneous catalysis

Suzuki–Miyaura coupling is a particularly important reaction in organic synthesis, since it is one of the most powerful tools for constructing a biaryl structure, which is present in many biologically active compounds, liquid crystals and electroluminescent materials.[1–3] However, when homogeneous palladium catalysts such as $Pd(PPh_3)_4$ or $Pd(PPh_3)_2Cl_2$ are used in the preparation of fine chemical products, we must address the problem of residual toxic metal in the product.[4] Furthermore palladium, which is increasingly expensive, cannot be recovered and reused. In contrast, heterogeneous catalysts can be easily separated from the reaction mixture by simple filtration and reused in successive reactions provided that the active sites have not become deactivated. Heterogeneous catalysis also helps to minimise waste derived from reaction workup, contributing to the development of green chemical processes.[5–8] From the standpoint of green and sustainable chemistry, development of immobilised palladium catalysts is challenging and important.[9–11] Recently, palladium complexes immobilised on cross-linked polymers[12–14] or silica gels[15–19] have been used as catalysts for the Suzuki–Miyaura reaction. However, these supported catalysts have generally suffered from some drawbacks such as limited mass transfer, low specificity and selectivity in addition to leaching of the catalytic species from the surface of the support[20] and some of these studies have been related to polymer-supported phosphine palladium catalysts.[12,21–23] It is well-known that transition-metal catalysts containing phosphine ligands are unstable[24–26] at high temperatures. Furthermore, the procedure for preparing the polymer-supported phosphine palladium complexes is rather complicated since the synthesis of the phosphine ligands usually requires multi-step sequences.

The development of new phosphine-free heterogeneous palladium complexes having a high activity and excellent recyclability is a topic of enormous importance. Our strategy was guided by three considerations: the heterogeneous ligand should be easily accessible (1), starting from readily available and inexpensive reagents (2). The heterogeneous palladium catalyst should ideally be air-stable, which should allow its storage in normal bottles with unlimited shelf life (3). The discovery of the mesoporous material MCM-41 has given an enormous stimulus to research in heterogeneous catalysis and has provided a new possible candidate for a solid support to immobilise homogeneous catalysts.[27–29] MCM-41 has a regular pore diameter of *ca.* 5 nm and a specific surface area >700 $m^2 g^{-1}$.[30] Considering the fact that the MCM-41 support has an ultrahigh surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of the MCM-41, we expect that an MCM-41-supported palladium catalyst will exhibit high catalytic activity and excellent reusability. So far, some functionalised MCM-41-supported palladium,[31–34] rhodium,[35] gold[36,37] and copper[38–41] complexes have been prepared and used successfully in organic reactions. In continuing our efforts to develop greener synthetic pathways for organic transformations, our new approach, described in this paper, was to design and synthesise a new MCM-41-immobilised nitrogen and sulfur mixed tridentate palladium(0) complex [MCM-41-2N,S-Pd(0)], which was used as an effective palladium catalyst for the Suzuki reaction of aryl bromides in air.

Results and discussion

Although the phosphine ligands can stabilise palladium and influence its reactivity, the simplest and cheapest palladium catalysts are of course phosphine-free systems, specifically when used in low loading. A new MCM-41-immobilised nitrogen and sulfur mixed tridentate palladium(0) complex [MCM-41-2N,S-Pd(0)] was synthesised from commercially readily available and inexpensive 3-(2-aminoethylamino) propyltrimethoxysilane by immobilisation on MCM-41, followed by reaction with thiophene-2-carboxaldehyde and $PdCl_2$ and then reduction with hydrazine hydrate (Scheme 1) (see SAFETY WARNING 1 in Experimental section). Small angle XRD analysis of the MCM-41-2N,S-Pd(0) indicated that, in addition to an intense diffraction peak (100), two higher order peaks (110) and (200) with lower intensities were detected and therefore the chemical bonding procedure did not diminish the structural ordering of the MCM-41.

Elemental analyses and X-ray photoelectron spectroscopy (XPS) were used to characterise the MCM-41-immobilised nitrogen and sulfur mixed tridentate palladium (0) catalyst. The S:Pd mole ratio of the MCM-41-2N,S-Pd(0) was determined to be 1.77, which is due to the fact that an excess of MCM-41-2N,S was used to react with $PdCl_2$ in the preparation of the MCM-41-2N,S-Pd(0) complex to achieve good stability and recyclability of the supported Pd(0) catalyst. The catalyst prepared in this way is referred to as MCM-41-2N,S-Pd(0) or the MCM-41-2N,S-Pd(0) complex and was used throughout this study. The XPS data for MCM-41-2N,S-Pd(0), MCM-41-2N,S-Pd(II), MCM-41-2N,S and $PdCl_2$ are listed in Table 1. It can be seen that the binding energies of Si_{2p}, N_{1s} and O_{1s} of MCM-41-2N,S-Pd(II)

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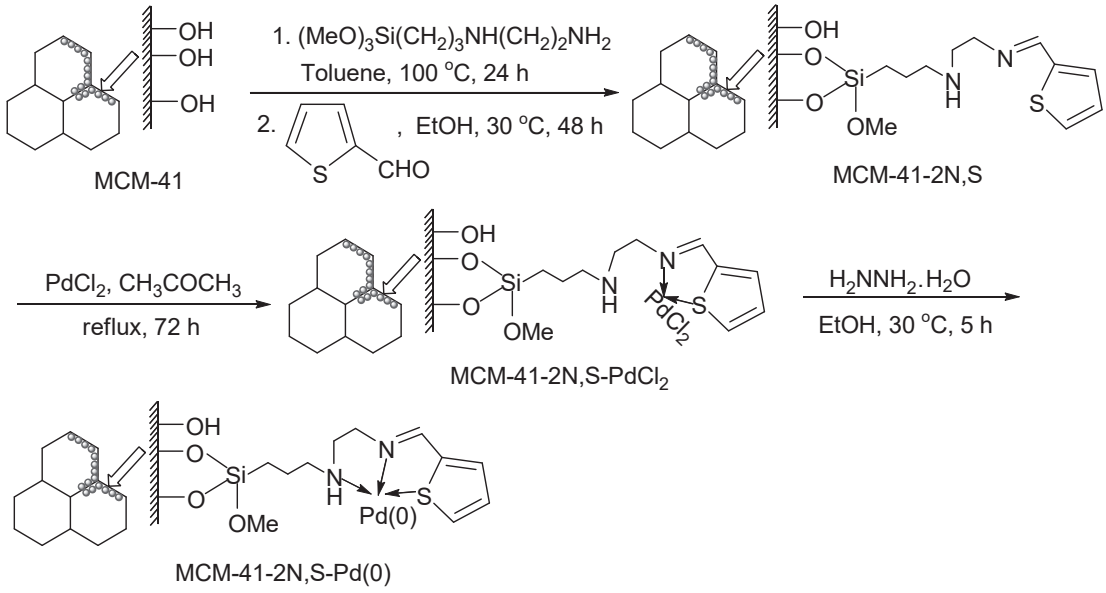


Scheme 1

are similar to those of MCM-41-2N,S and the binding energy of Cl_{2p} of MCM-41-2N,S-Pd(II) is similar to that of $PdCl_2$. However, the difference of $Pd_{3d5/2}$ binding energies between MCM-41-2N,S-Pd(II) and $PdCl_2$ is 0.7 eV. The difference of S_{2p} binding energies between MCM-41-2N,S-Pd(II) and MCM-41-2N,S is 0.5 eV. These results suggest that a coordination bond between S and Pd is formed in the MCM-41-2N,S-Pd(II). The binding energy (336.8 eV) of $Pd_{3d5/2}$ of MCM-41-2N,S-Pd(0) is lower than the binding energy (337.6 eV) of $Pd_{3d5/2}$ of MCM-41-2N,S-Pd(II). The $Pd_{3d5/2}$ binding energy depends strongly on the nature of the ligands. Consequently, it is impossible to identify the reduced complex as a zerovalent one on the basis of its $Pd_{3d5/2}$ binding energy only. However, the binding energy of Cl_{2p} in the MCM-41-2N,S-Pd(0) cannot be detected, the shift (lower) of $Pd_{3d5/2}$ binding energy together with the dark grey colour suggests that the reduction of the starting palladium(II) complex to the lower valent state has taken place. In addition, the difference of N_{1s} binding energies between MCM-41-2N,S-Pd(0) and MCM-41-2N,S is 0.7 eV. This result shows that a coordination bond between N and Pd is also formed in the MCM-41-2N,S-Pd(0), further confirming the reduction of the MCM-41-2N,S-Pd(II) to the MCM-41-2N,S-Pd(0). The MCM-41-2N,S-Pd(0) complex formed is stable in air for one month but for prolonged storage is better stored under an atmosphere of argon in which case no decomposition and deactivation are noted over the period of six months at room temperature. This result indicates that our consideration (3) has not been fully achieved by immobilisation of palladium(0) on MCM-41.

In our initial screening experiments, we carried out the Suzuki coupling of phenylboronic acid (1.5 equiv.) with 4-bromoanisole using MCM-41-2N,S-Pd(0) as the catalyst under various conditions to optimise the reaction conditions and the results are summarised in Table 2. Firstly, the base effect was examined by using 1 mol% of MCM-41-2N,S-Pd(0) as catalyst in DMF as solvent at 80 ºC. For the bases evaluated (K_3PO_4, Na_2CO_3, K_2CO_3, and Cs_2CO_3), K_2CO_3 was found to be the most effective (Table 2, entry 3). Among the solvents used (DMF, toluene, dioxane, xylene, and MeCN), xylene was found to be the best choice (Table 2, entry 7). Raising the reaction temperature shortened the reaction time, but did not increase the yield of 4-methoxybiphenyl (Table 2, entry 9). The reaction also proceeded smoothly at 60 ºC to afford the desired product

Table 1 Binding energies (eV) from XPS data for MCM-41-2N,S, MCM-41-2N,S-Pd(II), MCM-41-2N,S-Pd(0) and $PdCl_2$[a]

Sample	$Pd_{3d5/2}$	S_{2p}	N_{1s}	Si_{2p}	O_{1s}	Cl_{2p}
MCM-41-2N,S-Pd(0)	336.8	164.4	400.5	103.2	532.9	
MCM-41-2N,S-Pd(II)	337.6	164.3	399.9	103.3	533.1	199.3
MCM-41-2N,S		163.8	399.8	103.2	533.0	
$PdCl_2$	338.3					199.2

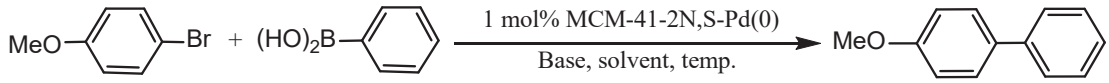
[a]The binding energies are referenced to C_{1s} (284.6 eV) and the energy differences were determined with an accuracy of ± 0.2 eV.

in excellent yield (Table 2, entry 10). Even if the amount of the catalyst was reduced to 0.5 mol%, the desired product could be obtained in 95% yield (Table 2, entry 11). We were pleased to find that the coupling reaction in air gave the same result as under Ar (Table 2, entry 12). The control experiments showed that no desired product was detected in the absence of a palladium catalyst (Table 2, entry 13). Taken together, an excellent result was obtained when the reaction was carried out with 0.5 mol% of the catalyst using K_2CO_3 as base in xylene at 60 °C in air (Table 2, entry 12).

To examine the scope for this heterogeneous palladium-catalysed Suzuki reaction, we have investigated the reaction using a variety of arylboronic acids and various aryl bromides as the substrates under the optimised reaction conditions (Scheme 2) and the results are listed in Table 3. To our delight, the Suzuki coupling reactions of aryl bromides having either electron-donating or electron-withdrawing groups with phenylboronic acid proceeded very smoothly at 60 °C to afford the corresponding coupled products **3a–c** in excellent yields (Table 3, entries 1–3). The reactions of sterically congested 2-bromotoluene and bulky 1-bromonaphthalene with phenylboronic acid also gave high yields of the desired products **3d** and **3e** respectively (Table 3, entries 4 and 5). Heteroaryl bromides such as 2-bromothiophene and 2-bromopyridine proved to be suitable substrates and gave the corresponding coupled products **3f** and **3g** in 87 and 89% yields respectively (Table 3, entries 6 and 7).

The optimised reaction conditions could be applied to the coupling reactions of some substituted phenylboronic acids with a variety of aryl bromides and the results are also listed in

Table 2 Optimisation of the coupling reaction of 4-bromoanisole with phenylboronic acid under various conditions[a]



Entry	Base	Solvent	Temp./ºC	Time/h	Yield/%[b]
1	K_3PO_4	DMF	80	3	61
2	Na_2CO_3	DMF	80	3	86
3	K_2CO_3	DMF	80	3	89
4	Cs_2CO_3	DMF	80	3	82
5	K_2CO_3	Toluene	80	3	90
6	K_2CO_3	Dioxane	80	3	74
7	K_2CO_3	Xylene	80	3	95
8	K_2CO_3	MeCN	80	3	65
9	K_2CO_3	Xylene	100	2	94
10	K_2CO_3	Xylene	60	4	96
11[c]	K_2CO_3	Xylene	60	8	95
12[c,d]	K_2CO_3	Xylene	60	8	95
13[e]	K_2CO_3	Xylene	60	24	0

[a]All reactions were performed using 4-bromoanisole (1.0 mmol), phenylboronic acid (1.5 mmol), MCM-41-2N,S-Pd(0) (1 mol%), base (2.0 mmol) in solvent (3.0 mL) under Ar.
[b]Isolated yield based on the 4-bromoanisole used.
[c]MCM-41-2N,S-Pd(0) (0.5 mol%) was used.
[d]In air.
[e]No palladium catalyst was used under Ar or in air.

Table 3. 4-Methylphenylboronic acid, 4-methoxyphenylboronic acid, 4-cyanophenylboronic acid and 4-chlorophenylboronic acid underwent coupling reactions with various aryl bromides effectively to furnish the desired coupling products **3h–q** in excellent yields (Table 3, entries 8–17). A wide range of electron-donating and electron-withdrawing groups such as methyl, methoxy, chloro, cyano, nitro, ketone and ester present in aryl bromides and arylboronic acids were well tolerated. Aryl chlorides were inert under the same conditions, giving only traces of cross-coupling products. To further illustrate that chloroarenes were inert in the reaction system, 4-chloro-4'-methylbiphenyl (**3i**) was selectively formed in 92% yield in the coupling reaction of 4-methylphenylboronic acid with 1-bromo-4-chlorobenzene (Table 3, entry 9). Bulky 1-naphthylboronic acid was also a suitable coupling partner and could undergo coupling reactions with aryl bromides to afford the desired coupled products **3e**, **3r** and **3s** in high yields (Table 3, entries 18–20). The Suzuki coupling reactions of sterically hindered arylboronic acids such as 2-methylphenylboronic acid and 2-trifluoromethylphenylboronic acid with aryl bromides also proceeded smoothly, affording the desired coupled products **3t–v** in good yields after 12 h (Table 3, entries 21–23). The present method provides a quite general route for the synthesis of unsymmetrical biaryls having various functionalities.

To determine whether the observed catalysis was due to the heterogeneous catalyst MCM-41-2N,S-Pd(0) or to a leached palladium species in solution, we performed a hot filtration test[42] on the coupling reaction of 4-bromoanisole with phenylboronic acid. The MCM-41-2N,S-Pd(0) complex was filtered off after 4 h of reaction time and the filtrate was allowed to react further by addition of K_2CO_3 (1 mmol). The catalyst filtration was performed at the reaction temperature (60 °C) in order to avoid possible recoordination or precipitation of soluble palladium upon cooling. We found that, after this hot filtration, no further reaction was observed, indicating that leached palladium species from the catalyst (if any) are not responsible for the observed activity. It was determined by inductively coupled plasma atom emission spectrometry (ICP-AES) analysis that no palladium could be detected in the hot filtered solution. This result suggests that the palladium catalyst remains on the support at elevated temperature during the reaction and points to a process heterogeneous in nature.

Table 3 Heterogeneous Suzuki reaction of aryl bromides with arylboronic acids catalysed by MCM-41-2N,S-Pd(0)[a]

Entry	Ar	Ar[1]	Time/h	Product	Yield/%[b]
1	4-$MeOC_6H_4$	Ph	8	**3a**	95
2	4-$MeCOC_6H_4$	P h	5	**3b**	93
3	4-$O_2NC_6H_4$	Ph	3	**3c**[c]	96
4	2-MeC_6H_4	Ph	7	**3d**	85
5	1-Naphthyl	Ph	6	**3e**	90
6	2-Thienyl	Ph	5	**3f**	87
7	2-Pyridyl	Ph	5	**3g**	89
8	4-PhC_6H_4	4-MeC_6H_4	8	**3h**	94
9	4-ClC_6H_4	4-MeC_6H_4	6	**3i**	92
10	2-Pyridyl	4-MeC_6H_4	5	**3j**	90
11	4-$O_2NC_6H_4$	4-$MeOC_6H_4$	4	**3k**	92
12	4-MeC_6H_4	4-$MeOC_6H_4$	6	**3l**	93
13	4-ClC_6H_4	4-NCC_6H_4	6	**3m**	89
14	4-MeC_6H_4	4-NCC_6H_4	7	**3n**	90
15	4-$MeOC_6H_4$	4-ClC_6H_4	8	**3o**	92
16	4-$MeCOC_6H_4$	4-ClC_6H_4	5	**3p**	96
17	4-$MeOCOC_6H_4$	4-ClC_6H_4	5	**3q**	91
18	Ph	1-Naphthyl	7	**3e**	88
19	4-ClC_6H_4	1-Naphthyl	6	**3r**	85
20	4-MeC_6H_4	1-Naphthyl	8	**3s**	83
21	3-MeC_6H_4	2-MeC_6H_4	12	**3t**	87
22	Ph	2-$CF_3C_6H_4$	12	**3u**	81
23	4-ClC_6H_4	2-MeC_6H_4	12	**3v**	86

[a]Reactions were carried out with aryl bromide (1 mmol), arylboronic acid (1.5 mmol), palladium catalyst (0.005 mmol), K_2CO_3 (2 mmol) in xylene (3.0 mL) at 60 ºC in air.
[b]Yield of isolated product **3** based on the aryl bromide.
[c]IMPORTANT: see SAFETY WARNING 2 in Experimental section.

For a heterogeneous precious catalyst system, it is important to examine its ease of separation, recoverability and reusability. This heterogeneous palladium catalyst can be easily recovered by simple filtration. We next investigated the possibility of reusing the catalyst on the coupling reaction of 4-bromoanisole

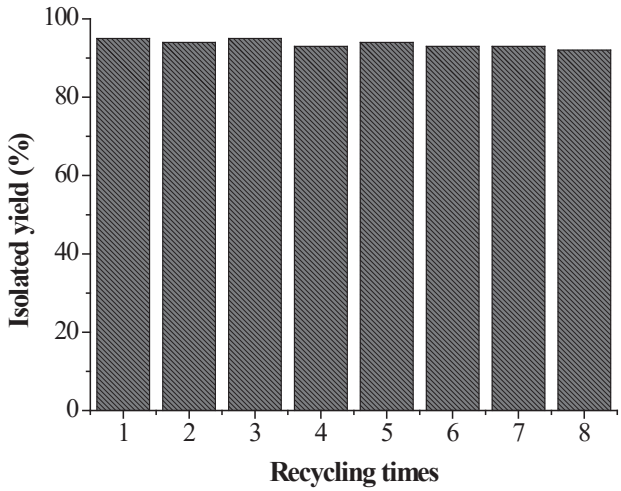


Fig. 1 Recycling of the MCM-41-2N,S-Pd(0) complex. Where 1 indicates the original catalyst before the first recycling.

with phenylboronic acid in air. After carrying out the reaction, the catalyst was separated by simple filtration and washed with distilled water, ethanol and diethyl ether. After being air-dried, it was reused directly without further purification. The recovered catalyst was used in the next run and almost consistent activity was observed for eight consecutive cycles (Fig. 1). The high stability and excellent reusability of the catalyst should result from the chelating action of nitrogen and sulfur mixed tridentate ligand on palladium and the mesoporous structure of the MCM-41 support. The result is important from industrial and environmental points of view.

In conclusion, we have developed a novel, phosphine-free, practical and economic catalyst system for the Suzuki reaction of aryl bromides with arylboronic acids by using an MCM-41-immobilised nitrogen and sulfur mixed tridentate palladium(0) complex [MCM-41-2N,S-Pd(0)] as catalyst. The advantages of our heterogeneous catalytic system over others are: (1) the preparation of the MCM-41-2N,S-Pd(0) catalyst is simple and convenient from reagents that are readily available commercially, (2) the reaction conditions are very mild, *i.e.* only 0.5 mol% palladium catalyst, air atmosphere and 60 °C and (3) excellent performance and reusability of the phosphine-free catalyst.

Experimental

All reagents were used as received without further purification. Xylene was a commercial mixture of isomers (CAS No. 1330-20-7). Toluene, chloroform and acetone were dried and distilled before use. The mesoporous material MCM-41 was prepared according to the literature procedure.[43] All reactions were carried out in air in oven-dried glassware with magnetic stirring. FTIR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer. ^{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. Palladium content was determined by ICP-AES on an Atomscan16 instrument (TJA Corporation). X-ray powder diffraction patterns were obtained on a Damx-rA instrument (Rigaku). X-ray photoelectron spectra were recorded on an XSAM 800 instrument (Kratos). Microanalyses were obtained using a PerkinElmer 240 elemental analyser.

Synthesis of MCM-41-2N,S

A solution of 3-(2-aminoethylamino)propyltrimethoxysilane (1.54 g) in dry chloroform (18 mL) was added to a suspension of MCM-41 (2.2 g) in dry toluene (180 mL). The mixture was stirred for 24 h at 100 °C. Then the solid was filtered off, washed with $CHCl_3$ (2 × 20 mL) and dried under reduced pressure at 160 °C for 5 h. The dried white solid (1.73 g) was then reacted with thiophene-2-carboxaldehyde (0.263 g, 2.32 mmol) in dry ethanol (10 mL) at 30 °C for 48 h. The solid product was filtered off, washed with ethanol (3 × 20 mL) and diethyl ether (20 mL) and dried under reduced pressure at 120 °C for 5 h to obtain the hybrid material MCM-41-2N,S (1.834 g). The nitrogen and sulfur contents were found to be 1.62 mmol g^{-1} and 0.79 mmol g^{-1} respectively by elemental analysis.

Preparation of MCM-41-2N,S-Pd(0) complex

SAFETY WARNING 1: Appropriate precautions must be taken when using hydrazine hydrate as it is highly toxic and harmful to health.

In a small Schlenk tube, the above-functionalised MCM-41 (MCM-41-2N,S) (1.81 g, 1.43 mmol of S) was mixed with $PdCl_2$ (0.143 g, 0.81 mmol) in dry acetone (40 mL). The mixture was refluxed for 72 h under an argon atmosphere. The product was allowed to cool and was then filtered off. The yellow solid was washed with distilled water (3 × 20 mL) and acetone (2 × 20 mL) and then stirred with hydrazine hydrate (1.5 g) and EtOH (25 mL) at 30 °C under Ar for 5 h. The resulting product was filtered off, washed with EtOH (3 × 20 mL) and Et_2O (2 × 20 mL) and dried under reduced pressure at 60 °C for 5 h to give a grey catalyst material [MCM-41-2N,S-Pd(0)] (1.854 g). The palladium content was found to be 0.41 mmol g^{-1}.

Suzuki reaction of aryl bromides with arylboronic acids; general procedure

A mixture of aryl bromide (1.0 mmol), arylboronic acid (1.5 mmol), potassium carbonate (2.0 mmol), xylene (3 mL) and the MCM-41-2N,S-Pd(0) complex (13 mg, 0.005 mmol of Pd) was stirred at 60 °C under air for 3–12 h. The mixture was cooled and the MCM-41-2N,S-Pd(0) complex was filtered off. It was then washed with distilled water (2 × 10 mL), EtOH (2 × 10 mL) and Et_2O (2 × 10 mL). The filtrate was poured into a saturated aqueous NaCl solution (50 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The extracts were washed with water (3 × 20 mL) and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica gel using hexane or hexane/ethyl acetate (15:1 to 20:1) as eluent.

4-Methoxybiphenyl (**3a**): White solid; m.p. 88–90 °C (lit.[44] 81–83 °C); IR (KBr): 1607, 1489, 1252, 1039, 759, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.50 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33–7.29 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 140.8, 133.8, 128.7, 128.2, 126.8, 126.7, 114.2, 55.4.

4-Acetylbiphenyl (**3b**): White solid; m.p. 117–118 °C (lit.[44] 116–118 °C); IR (KBr): 2999, 1682, 1602, 1265, 962, 767 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.71–7.63 (m, 4H), 7.49–7.37 (m, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 145.8, 139.9, 135.9, 129.0, 128.9, 128.2, 127.3, 127.2, 26.7.

4-Nitrobiphenyl (**3c**)*:*

SAFETY WARNING 2: The manufacture and use for all purposes of the compound **3c** is prohibited in the UK by the Control of Substances Hazardous to Health (COSHH) regulations. 4-Nitrobiphenyl (**3c**) is a potent human carcinogen and the *Journal of Chemical Research* strongly advises against its preparation.

Yellow solid; m.p. 113 °C (lit.[44] 109–111.5 °C); IR (KBr): 1597, 1576, 1515, 1345, 854, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.63–7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 147.1, 138.8, 129.2, 128.9, 127.8, 127.4, 124.1.

2-Methylbiphenyl (**3d**): Colourless oil;[44] IR (neat): 3061, 3022, 2956, 1479, 1382, 865, 749, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.21 (m, 9H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 135.4, 130.3, 129.8, 129.2, 128.1, 127.3, 127.2, 126.8, 125.8, 20.5.

1-Phenylnaphthalene (**3e**): Colourless oil;[45] IR (neat): 3056, 1592, 1507, 1494, 1395, 762, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.89–7.82 (m, 3H), 7.53–7.40 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 140.3, 133.8, 131.7, 130.1, 128.3, 127.7, 127.3, 127.2, 127.0, 126.1, 126.0, 125.8, 125.4.

2-Phenylthiophene (**3f**): White solid; m.p. 36–37 °C (lit.[46] 37–38 °C); IR (KBr): 3073, 1601, 1532, 1489, 1446, 1256, 851, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.56 (m, 2H), 7.35–7.18 (m, 5H), 7.04–7.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 134.5, 129.0, 128.2, 127.6, 126.1, 124.9, 123.2.

2-Phenylpyridine (**3g**): Colourless oil;[46] IR (neat): 3061, 1587, 1564, 1469, 1449, 745, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 4.8 Hz, 1H), 7.98–7.96 (m, 2H), 7.69–7.67 (m, 2H), 7.47–7.36 (m, 3H), 7.18–7.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 149.5, 139.4, 136.8, 129.0, 128.8, 127.0, 122.2, 120.6.

4-*(4-Methylphenyl)biphenyl* (**3h**): White solid; m.p. 207–208 °C (lit.[47] 208–209 °C); IR (KBr): 3029, 1642, 1567, 1481, 1145, 816, 765 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.60 (m, 6H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.26–7.21 (m, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 140.1, 139.8, 137.8, 137.2, 135.7, 129.6, 128.8, 127.5, 127.3, 127.1, 126.9, 21.2.

4-Chloro-4'-methylbiphenyl (**3i**): White solid; m.p. 121–123 °C (lit.[48] 122–123 °C); IR (KBr): 3027, 1641, 1480, 1069, 954, 809 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 137.4, 137.1, 133.0, 129.6, 128.8, 128.2, 126.8, 21.1.

2-(4-Methylphenyl)pyridine (**3j**): Colourless oil;[46] IR (neat): 3010, 2921, 1615, 1588, 1466, 1432, 1185, 829, 774 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67–8.64 (m, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.66–7.63 (m, 2H), 7.26–7.21 (m, 2H), 7.16–7.12 (m, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 149.7, 149.6, 138.9, 136.7, 129.5, 126.8, 121.8, 120.2, 21.3.

4-Methoxy-4'-nitrobiphenyl (**3k**): Yellow solid; m.p. 99–100 °C (lit.[48] 100–102 °C); IR (KBr): 2957, 1602, 1595, 1512, 1345, 1187, 1109 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 147.2, 146.6, 131.1, 128.6, 127.1, 124.2, 114.6, 55.4.

4-Methoxy-4'-methylbiphenyl (**3l**): White solid; m.p. 110–112 °C (lit.[48] 110–111 °C); IR (KBr): 2916, 1609, 1503, 1289, 1251, 1039, 809 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.27–7.21 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 138.0, 136.4, 133.8, 129.5, 128.0, 126.6, 114.2, 55.4, 21.1.

4-Chloro-4'-cyanobiphenyl (**3m**): White solid; m.p. 125–127 °C (lit.[49] 125–127 °C); IR (KBr): 2227, 1641, 1563, 1486, 1146, 1091, 952, 857 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 137.6, 135.0, 132.7, 129.3, 128.5, 127.6, 118.7, 111.3.

4-Cyano-4'-methylbiphenyl (**3n**): White solid; m.p. 106–108 °C (lit.[48] 107–109 °C); IR (KBr): 2226, 1642, 1605, 1564, 1494, 1146, 852, 815 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 138.8, 136.3, 132.6, 129.8, 127.5, 127.1, 119.1, 110.5, 21.2.

4-Chloro-4'-methoxybiphenyl (**3o**): White solid; m.p. 122–123 °C (lit.[48] 123–124 °C); IR (KBr): 2962, 1607, 1484, 1291, 1264, 1199, 823, 814 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.46 (m, 4H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 139.3, 132.7, 132.5, 128.9, 128.1, 128.0, 114.3, 55.4.

4-Acetyl-4'-chlorobiphenyl (**3p**): White solid; m.p. 104–105 °C (lit.[50] 102–103 °C); IR (KBr): 2962, 1676, 1601, 1479, 1269, 1099, 816 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–8.01 (m, 2H), 7.66–7.63 (m, 2H), 7.57–7.53 (m, 2H), 7.45–7.41 (m, 2H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 144.5, 138.3, 136.1, 134.5, 129.2, 129.0, 128.5, 127.1, 26.7.

4-Chloro-4'-methoxycarbonylbiphenyl (**3q**): White solid; m.p. 94 °C (lit.[48] 94 °C); IR (KBr): 2959, 1726, 1609, 1481, 1106, 826, 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 144.3, 138.4, 134.3, 130.9, 130.2, 129.1, 128.5, 126.9, 52.2.

1-(4-Chlorophenyl)naphthalene (**3r**): Colourless oil;[45] IR (neat): 3059, 1597, 1506, 1489, 1394, 1089, 1016, 839, 799, 775 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.81 (m, 3H), 7.47–7.32 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.2, 139.0, 133.9, 133.4, 131.5, 128.6, 128.5, 128.1, 127.0, 126.4, 126.0, 125.8, 125.5.

1-(4-Methylphenyl)naphthalene (**3s**): White solid; m.p. 48–50 °C (lit.[45] 52–53 °C); IR (KBr): 3046, 2921, 1592, 1505, 1396, 1022, 823, 799, 775 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.53–7.38 (m, 6H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 137.9, 137.0, 133.9, 131.8, 130.0, 129.0, 128.3, 127.5, 127.0, 126.2, 126.0, 125.8, 125.5, 21.3.

2-Methyl-3'-methylbiphenyl (**3t**): Colourless oil;[44] IR (neat): 3023, 2922, 1515, 1382, 825, 759, 729 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.11 (m, 8H), 2.37 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 141.8, 137.5, 135.2, 130.2, 129.9, 129.7, 127.9, 127.4, 127.1, 126.2, 125.6, 21.4, 20.4.

2-(Trifluoromethyl)biphenyl (**3u**): Colourless oil;[44] IR (neat): 3067, 3032, 1682, 1602, 1316, 1129, 1036, 767, 749, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.83 (m, 1H), 7.66–7.41 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 140.2, 132.4, 131.6, 129.3, 129.2, 128.1, 127.9, 127.6, 126.3, 122.7.

4-Chloro-2'-methylbiphenyl (**3v**): Colourless oil;[51] IR (neat): 3022, 1657, 1596, 1479, 1093, 1008, 835, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.35 (m, 2H), 7.26–7.16 (m, 6H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 140.4, 135.3, 132.8, 130.5, 130.4, 129.7, 128.3, 127.6, 125.9, 20.4.

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