▌Heterogeneous Catalysis

C-2 Selective Arylation of Indoles with Heterogeneous Nanopalladium and Diaryliodonium Salts

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Abstract: A simple and efficient method to prepare synthetically useful 2-arylindoles is presented, using a heterogeneous Pd catalyst and diaryliodonium salts in water under mild conditions. A remarkably low leaching of metal catalyst was observed under the applied conditions. The developed protocol is highly C-2 selective and tolerates structural variations both in the indole and in the diaryliodonium salt. Arylations of both *N*–H indoles and *N*-protected indoles with *ortho*-substituted, electron-rich, electron-deficient, or halogenated diaryliodonium salts were achieved to give the desired products in high to excellent isolated yields within 6 to 15 h at room temperature or 40 °C.

2-Arylindoles are an important class of building blocks for the synthesis of various potential drug candidates and natural products.[1] Palladium-catalyzed cross-coupling reactions have proved to be an excellent method to produce these kinds of building blocks from pre-functionalized reagents.[2] A direct transformation of a C–H bond to a C–C bond, without any pre-functionalization, provides a greater simplicity and efficiency in the preparation of 2-arylindoles. Recently, several innovative strategies have been developed for direct C-2 arylation of indoles.[3] Nevertheless, the need for large catalyst amounts (5–10 mol%), elevated temperatures ($\geq$80 °C), poor recyclability of the catalyst and/or the use of harmful solvents or additives remain as major concerns that need solutions. Milder conditions may be used if diaryliodonium salts are employed, and selective C-2 arylation of indoles was achieved by using Pd cat-

alysis, as demonstrated by Sanford and co-workers and recently also described by Glorious and co-workers.[4] Cu-catalyzed C-3 or C-2 arylation with diaryliodonium salts was later reported by Gaunt and co-workers.[5] Ackermann's group showed that C-3 arylation of indoles can be obtained under metal-free conditions using diaryliodonium salts at high temperatures.[6] Recently, Glorious and co-workers reported that commercially available Pd/C can be used in the C–H functionalization of heteroaromatic compounds.[4b, 7] Ferromagnetic nanoparticles in combination with boronic acids has also been reported for 2-arylation of indoles under mild conditions,[3a] however, this protocol requires additives and external oxidants.

Homogeneous catalysis is generally associated with the requirement of additional purification steps to remove trace amounts of metal impurities from the final product and difficulties in recycling of the catalyst. Heterogeneous catalysis, on the contrary, offers a simple solution to these drawbacks. Over the past few years, metal nanoparticles have emerged as a more attractive alternative compared to traditional methods for catalysis, as they have large surface areas and high density of unsaturated coordination sites.[8] The Bäckvall group has recently reported on the preparation and application of a heterogeneous catalyst based on Pd nanoparticles supported on amino-functionalized mesocellullar foam, Pd⁰-AmP-MCF (Figure 1a and b).[9] This nanocatalyst has proven to be powerful in a diverse set of organic transformations with high recyclability and low leaching.[9, 10] The efficiency of the catalyst can be ascribed to the small and well-dispersed palladium particles with a size range of 2–3 nm and to the morphology of the siliceous mesoporous (MCF) material, which has a three-dimensional network of pores with windows, enabling high surface areas.[11] More recently, applications of the closely related heterogeneous Pd^II catalyst, Pd^II-AmP-MCF (Figure 1c) have also been reported by the group.[12] With the aim of widening the scope of our Pd-AmP-MCF, we set out to investigate the 2-arylation of indoles using non-toxic diaryliodonium salts,[13] which can be obtained by simple one-pot procedures developed by the Olofsson group.[14] Herein, we report a mild and straightforward route to obtain selective C-2 arylation of indoles in water using a combination of nanopalladium and diaryliodonium salts.

To find the optimal conditions for the reaction, a screening of different reaction parameters was initiated by using indole (**1a**), diphenyliodonium salts **2**, and Pd^II-AmP-MCF as catalyst (Table 1). The yield of 2-phenyl-1*H*-indole (**3a**) was quantified by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as in-

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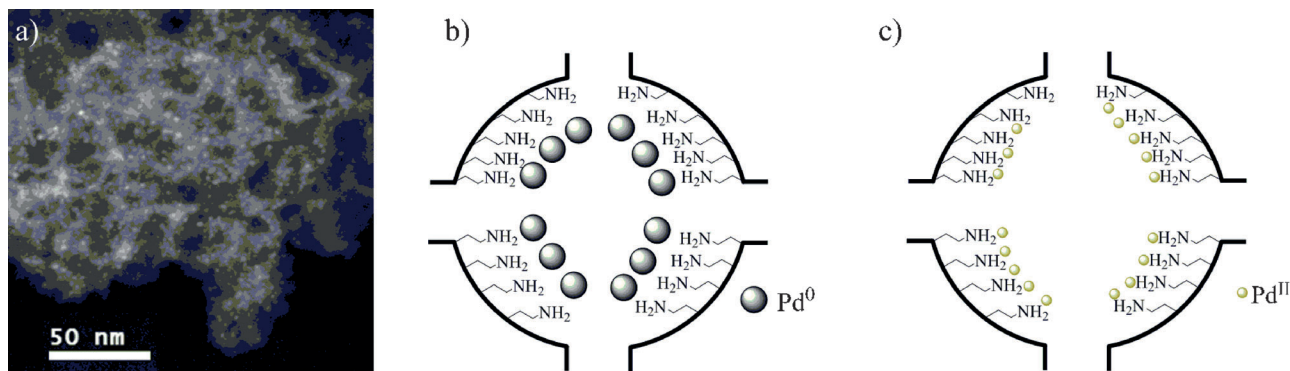
Figure 1. a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Pd[0]-AmP-MCF b) a schematic view of Pd[0]-AmP-MCF and c) a schematic view of Pd[II]-AmP-MCF.

Table 1. Optimization.[a]

Entry	Salt 2	X	Solvent	Time [h]	Yield [%][b]
1	2a	BF$_4$	THF	15	11
2	2a	BF$_4$	PhMe	15	0
3	2a	BF$_4$	CH$_2$Cl$_2$	15	29
4	2a	BF$_4$	EtOAc	15	0
5	2a	BF$_4$	AcOH	15	79
6	2a	BF$_4$	H$_2$O	15	91
7	2a	BF$_4$	EtOH	15	0
8	2b	OTs	H$_2$O	15	92
9	2c	OTf	H$_2$O	15	0[c]
10	2a	BF$_4$	H$_2$O	6	88
11	2b	OTs	H$_2$O	6	26

[a] Reaction conditions: Indole (0.2 mmol), Ph$_2$IX (0.4 mmol), and Pd[II]-AmP-MCF (0.009 mmol, with respect to Pd content) were suspended in 2 mL solvent and the reaction was stirred at room temperature. [b] Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [c] Compound 3a was obtained in 56% yield with triflate 2c when the reaction was run in AcOH instead of water.

Table 2. Investigation of the catalyst and reaction stoichiometry.[a]

Entry	Catalyst	Loading [mol%]	Time [h]	Yield [%][b]
1	Pd[II]-AmP-MCF	4.5	3	63
2	Pd[0]-AmP-MCF	4.5	3	91
3	Pd/C (10 wt%)	2.5	6	0
4	Pd[0]-AmP-MCF	2.5	6	91[c]
5	Pd[0]-AmP-MCF	1	14	79
6[d]	Pd[0]-AmP-MCF	4.5	3	50
7[d]	Pd[0]-AmP-MCF	4.5	6	93
8[e]	Pd[0]-AmP-MCF	2.5	6	0

[a] Reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), and catalyst were suspended in 2 mL solvent and the reaction was stirred at room temperature. [b] Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. [c] Isolated yield. [d] 1.1 equiv of 2a was used. [e] The reaction was performed with PhI (2 equiv) instead of 2a.

ternal standard. The investigation commenced with a solvent screen, which revealed that the solvent had a major impact on the yield, while the reaction was completely C-2 selective in all cases. The product formation was very poor in aprotic solvents such as THF, toluene, CH$_2$Cl$_2$, and EtOAc (Table 1, entries 1–4), whereas the protic solvents AcOH and H$_2$O resulted in significantly increased yields of 3a (Table 1, entries 5 and 6). Surprisingly, only starting material was recovered when the reaction was run in EtOH (Table 1, entry 7).[4b] Hence, water was selected as the optimal solvent based on both yield and environmental aspects.

Subsequently, the effect of the anion in iodonium salts 2 was evaluated. Tetrafluoroborate 2a and tosylate 2b delivered indole 3a in similar yields (Table 1, entries 6 and 8), whereas reactions with triflate 2c delivered no product (Table 1, entry 9). When the reaction time was reduced to 6 h, tetrafluoroborate 2a proved to be more efficient than tosylate 2b, with product

formation in 88 versus 26% yield (Table 1, entries 10 and 11). The explanation for these observations could be ascribed to the different coordination abilities of the anions to the metal center. Since tetrafluoroborate is a very weakly coordinating ligand, the palladium intermediate with tetrafluouoroborate should be more reactive than those with tosylate or triflate as anions.

The catalyst type, loading, and influence on the reaction time were subsequently investigated (Table 2). Both Pd[0] and Pd[II] have proven successful in C-2 arylation of indoles, and the catalytic activity of our nanopalladium catalyst, Pd[0]-AmP-MCF, was therefore compared with that of Pd[II]-AmP-MCF. The reaction time was shortened to 3 h to reveal any difference in activity between the two catalysts. It was found that Pd[II]-AmP-MCF gave 3a in 63% yield (Table 2, entry 1). Surprisingly, Pd[0]-AmP-MCF afforded 3a in excellent yield within this short reaction time (Table 2, entry 2). Employing the commercially available Pd/C (10 wt%) under the same reaction conditions did not result in product formation (Table 2, entry 3).[4b] In Pd[0]-AmP-MCF, the Pd species are clustered together in well-defined nanoparticles that are coordinated to aminopropyl

groups, which is not the case in Pd/C. This might be the reason for the observed difference in reactivity. Mechanistically, diaryliodonium salts used with Pd[II] are known to undergo a Pd[II]/Pd[IV] cycle,[15] and this is the most viable reaction pathway even in the reactions with Pd[0]-AmP-MCF.

When the catalyst loading was decreased to 2.5 mol%, **3a** was obtained in 91% yield within 6 h, whereas 1 mol% catalyst loading resulted in reduced conversion even with prolonged reaction times (Table 2, entries 4 and 5). As a last step of the optimization process, an experiment with 1.1 equiv of salt **2a** and 4.5 mol% catalyst was performed. Indole **3a** was formed in 50% yield within 3 h, and prolongation of the reaction time to 6 h afforded **3a** in 93% yield (Table 2, entries 6 and 7). For comparative reasons, one reaction was performed with 2 equiv of PhI instead of **2a** with the other parameters unchanged. As expected, product formation could not be observed (Table 2, entry 8). Arguing that it is more desirable to have a lower catalyst loading (2.5 mol%) with a reasonable reaction time (6 h) than using less iodonium salt, the substrate scope was investigated with 2.5 mol% Pd[0]-AmP-MCF and 2 equiv of diaryliodonium salt at room temperature for 6 h.

A series of indoles **1** were next reacted with diphenyliodonium salt **2a** to evaluate the generality of the method (Scheme 1). To our delight, variously substituted indoles could
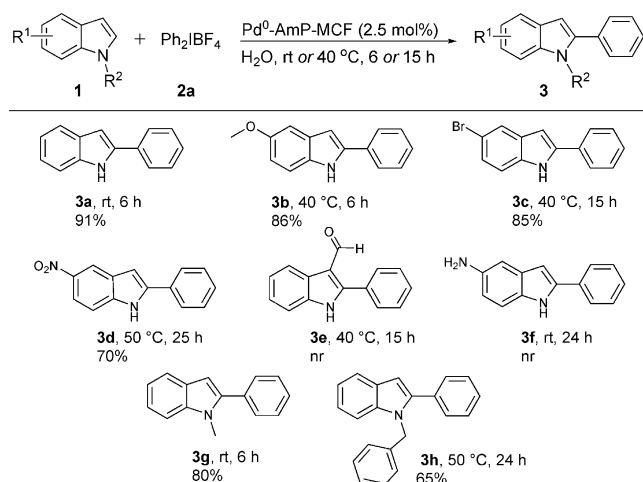

Scheme 1. Phenylation of substituted indoles.

be phenylated by using the developed catalytic system with only small changes in reaction times and temperatures. The electron-rich *N*–H indole **3b** was obtained in 86% yield at a slightly elevated temperature (40 °C), and synthesis of the bromo-substituted *N*–H indole **3c** was achieved in equally high yield. This product is of particular interest as the bromide can function as a handle for further functionalization. In addition, the bromide can trigger undesired side reactions in the presence of metal catalysts, and consequently, only a few C-2 arylations of this substrate are reported.[3h, i, 4a]

We subsequently investigated a selection of substituted *N*–H indoles that have not been reported in C-2 arylations. To our delight, a highly electron-withdrawing nitro group was well

tolerated (**3d**, 70% yield). Indole-3-carboxaldehyde was, on the other hand, inert under the reaction conditions, which might be explained by steric hindrance. The synthesis of aminoindole **3f** was also unsuccessful. *N*-Protected indoles are usually arylated more easily than *N*—H indoles.[3] Indeed, the *N*-methylated indole **3g** was obtained in 80% yield at room temperature. On the contrary, reactions with *N*-benzylated indole were sluggish, and provided **3h** in 65% yield after prolonged reaction time at 50 °C. Indoles with TBDMS or Boc protecting groups were inert under the reaction conditions, indicating that the reaction is sensitive to steric hindrance or electronic deactivation.
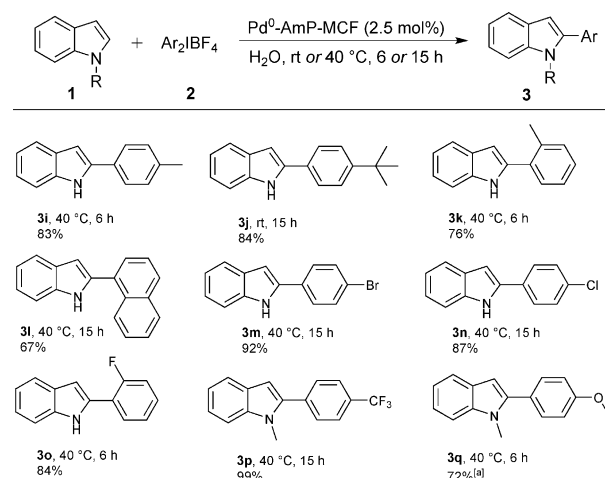
Substituted diaryliodonium salts **2** were subsequently employed in the arylation of *N*-H indole **1a**. The chemoselectivity in arylations with unsymmetrical diaryliodonium salts has previously been investigated,[16] and the groups of Sanford and Gaunt have demonstrated that mesityl (Mes) or 2,3,5-triisopropylphenyl (TRIP) groups can be used as "dummy groups" in metal-catalyzed arylations.[5, 15a] Mesityl salt **2d** and TRIP salt **2e** were thus evaluated in the C-2 arylation of indoles (Scheme 2).
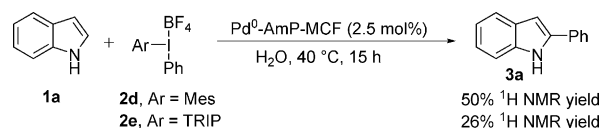
Scheme 2. Chemoselectivity with unsymmetrical diaryliodonium salts.

The phenyl group was indeed chemoselectively transferred, but in substantially lower yields compared to the model reaction using salt **1a**, despite prolonged reaction time at 40 °C.

Hence, symmetric diaryliodonium salts were used in the scope study, and high to excellent yields were obtained with various iodonium salts upon increasing the reaction temperature to 40 °C (Scheme 3). 4-Alkyl-substituted iodonium salts were successfully employed to yield products **3i** and **3j** in


Scheme 3. Arylation scope with substituted diaryliodonium salts. [a] The isolated crude product (79%) was contaminated with 7% of homocoupled anisole, which gives 72% yield of **3q**.

83% and 84%, respectively. Steric hindrance in the *ortho*-position of the salt only had a minor impact on the outcome as compound **3k** was obtained in 76% yield. Even a sterically congested naphthyl salt could be utilized in the reaction to provide **3l**.

Halogenated diaryliodonium salts were successfully employed, giving products **3m–3o** in high to excellent yields upon prolonged reaction time. Arylation with an electron-deficient CF$_3$-substituted salt was highly efficient, and the arylated product **3p** was isolated in 99% yield. Synthesis of the electron-rich indole **3q** was achieved in 72% yield, unfortunately with 7% inseparable impurity of 4,4′-dimethoxy-1,1′-biphenyl. Arylation of *N*-H indole **1a** with the trifluoromethyl or methoxy salts could not be achieved. The reaction was completely regioselective with all substrates, yielding only C-2 arylated products. Surprisingly, no C-3 phenylated indole was detected even when iodonium salt **1a** was reacted with 2-methyl indole under the optimized conditions, further illustrating the regioselectivity of the process. Compared to Sanford's arylation,[4a] the present reaction shows higher tolerance towards *N*—H indoles with lower catalyst loadings.

One advantage with heterogeneous catalysis is the ease of recycling and reuse of the catalyst compared to homogeneous catalysis. With that in mind, the recyclability of Pd^0-AmP-MCF was investigated in the model reaction (Scheme 4). The cata-
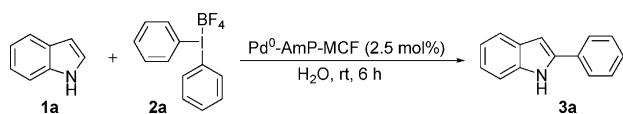
Scheme 4. Conditions for investigation of the recyclability of the catalyst.

lyst proved to be active in three subsequent cycles, although a gradual decrease in activity was observed for each cycle (100%, 80%, 67%).[17] This might be due to dispersion of Pd species away from the nanoclusters to the aminopropyl groups on the MCF. This could well be the reason why Pd^{II}-AmP-MCF was less active than Pd^0-AmP-MCF.

The amount of leached metal catalyst into the solution is a typical concern in heterogeneous catalysis. Therefore the leaching of Pd species into the solution was determined under the optimized reaction conditions (Scheme 4). After the indicated reaction time, the solid-free filtrate was analyzed by elemental analysis (ICP-OES) for palladium content. Gratifyingly, a very low leaching of 0.6 ppm was detected for the presented catalytic system. A control experiment with the leached palladium (0.6 ppm) was performed to ensure that it did not participate in the catalytic reaction, and satisfyingly only the starting material was recovered in this experiment.

To summarize, we have developed a highly C-2 selective arylation of indoles using a heterogeneous Pd catalyst and diaryliodonium salts in water under mild conditions. The catalytic system exhibited a very low leaching (0.6 ppm) and was compatible with both *N*-H indoles and *N*-protected indoles with various substituents. The protocol also tolerated variations of the diaryliodonium salt and the use of *ortho*-substituted, elec-

tron-rich, electron-deficient, and halogenated salts afforded the C-2 arylated indoles in high to excellent yields.

Experimental Section

General procedure for arylation of indoles 1: Diaryliodonium tetrafluoroborate **2** (1 mmol, 2 equiv), Pd^0-AmP-MCF (0.0125 mmol, 2.5 mol%), and indole **1** (0.5 mmol) were added to a vial followed by the addition of H$_2$O (2 mL). The reaction was stirred at the indicated time and temperature. The reaction mixture was then filtered through a pad of celite, extracted with CH$_2$Cl$_2$ (2×10 mL), dried over MgSO$_4$, filtered, and concentrated in vacuo. The crude reaction mixture was purified by column chromatography to yield 2-aryl-1*H*-indole **3**.

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[17] Additional experiments to improve the recycling were performed, see the Supporting Information.