Covalently Stabilized Pd Clusters in Microporous Polyphenylene: An Efficient Catalyst for Suzuki Reactions Under Aerobic Conditions

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A novel catalyst composed of a microporous polyphenylene network and covalently stabilized Pd clusters (Pd/MPP) for highly efficient Suzuki–Miyaura coupling is synthesized with an in-situ one-pot chemical approach, through the catalytic trimerization of 1,3,5-triethynylbenzene. The unique Pd/MPP cluster exhibits very high catalytic activity for a broad scope of Suzuki–Miyaura reactions with short reaction time, good yield, and high turnover number and turnover frequency values, even in aqueous media under aerobic conditions. The strong covalent interaction between Pd and MPP network prevents the agglomeration or leaching of Pd clusters and enables the catalyst to remain highly active, even after a number of cycles.

1. Introduction

Suzuki–Miyaura coupling reaction is one of the most important reactions for the synthesis of biaryl compounds, which has been widely used for various industry applications.[1] Conventionally, highly air-sensitive catalysts such as $Pd(PPh_3)_4$ and toxic solvents like benzene are used in the reaction. As a result, restrict reaction conditions, such as air-free and sealed systems, have to be used. In addition, the catalyst is difficult to be separated and recycled. In order to overcome these problems, Pd nanoparticles are combined with various supports including porous silica dioxide,[2,3] metal oxides,[4,5] carbon structures,[6,7] polymers,[8,9] and dendrimers[10,11] to develop heterogeneous catalysts.[12]

Microporous organic materials, including metal organic frameworks (MOFs),[13–16] covalent organic frameworks (COFs),[17–20] and conjugated microporous polymers (CMPs),[21–23] are one class of promising candidates for well-defined catalyst supports. A distinct advantage of these microporous organic materials is the versatile potential to adjust their structures and properties by rational design of different building blocks with a range of function groups. Particularly, CMPs are more attractive since they hold highly stable skeletons and amorphous structures which are reliable in various catalytic reactions even in harsh conditions. Regrettably, the study of CMPs as catalyst supports is rare.[24,25]

In general, supported palladium catalysts are prepared by immersing supports in the solution of palladium salt followed with reduction to deposit Pd particles into pores of the supports. Unfortunately, this simple method is not suitable for the supports based on microporous organic materials since there are many drawbacks which significantly decline the activity of the catalysts: 1) the Pd nanoparticles are easy to agglomerate and to be washed away during reaction processing and catalyst recycling, because the Pd-support interaction is not strong enough; 2) the pore size distribution and the surface area of the support is changeable along with the post treatment.[25–27] Recently, Cooper et al.[28] investigated the supercritical fluid processing technique to attach palladium nanoparticles into CMPs so that the interaction between Pd particles and the support was believed to be stronger. Thomas et al. developed an efficient method to distribute uniform metal particles into CMPs by for instance importing pre-synthesized Pd clusters into covalent triazine framework.[29] Despite of these pioneering research works, it still appears to be rather challenging to develop controllable methods which can introduce stabilized nanoparticles into CMP networks and in the meantime keep the well-defined

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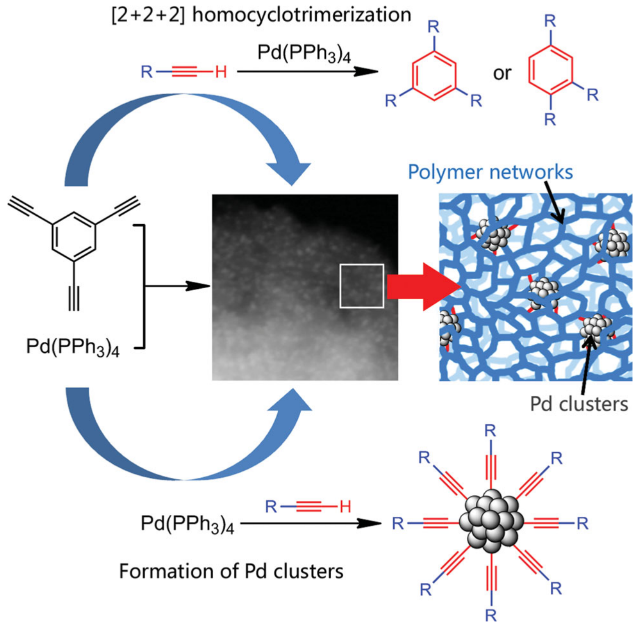

Figure 1. Schematic outline for the preparation of Pd/MPP clusters.

porosity structure of CMPs. Herein, we report a novel in-situ chemical approach with which the formation of CMP support and the importation of Pd clusters are successfully realized in one step, resulting in a unique Pd/CMP hybrid with well-defined porosity and monodispersed Pd clusters. More importantly, the Pd clusters are covalently linked with the CMP networks, forming a highly stabilized Pd/CMP catalyst which shows excellent catalytic activity and stability for Suzuki reactions even in aerobic conditions.

2. Results and Discussion

2.1. Synthetic Route

The synthetic route is shown in **Figure 1**. Being catalyzed by $Pd(PPh_3)_4$, the 1,3,5-triethynylbenzene (TEB) is trimerizated into polyphenylene network by [2 + 2 + 2] homocyclotrimerization of alkynes.[30] And simultaneously, $Pd(PPh_3)_4$ is decomposed and aggregated into alkyne-protected Pd clusters, which is similar with the Au clusters stabilized by phenylacetylene reported by Maity etc. (Figure S1 and S2).[31] Immediately, Pd clusters are stabilized and encapsulated by continuously extending microporous polymer skeletons, resulting in palladium cluster-functionalized conjugated microporous polyphenylene (Pd/MPP) in one step.

2.2. Characterization of Pd/MPP

The synthesis process is investigated by Fourier transform infrared spectroscopy (FT-IR). As shown in **Figure 2**a, after reaction, the peaks at 3280 cm^{-1} ($\equiv C-H$ stretching) and 2109 cm^{-1} ($C\equiv C$ stretching) which can be attributed

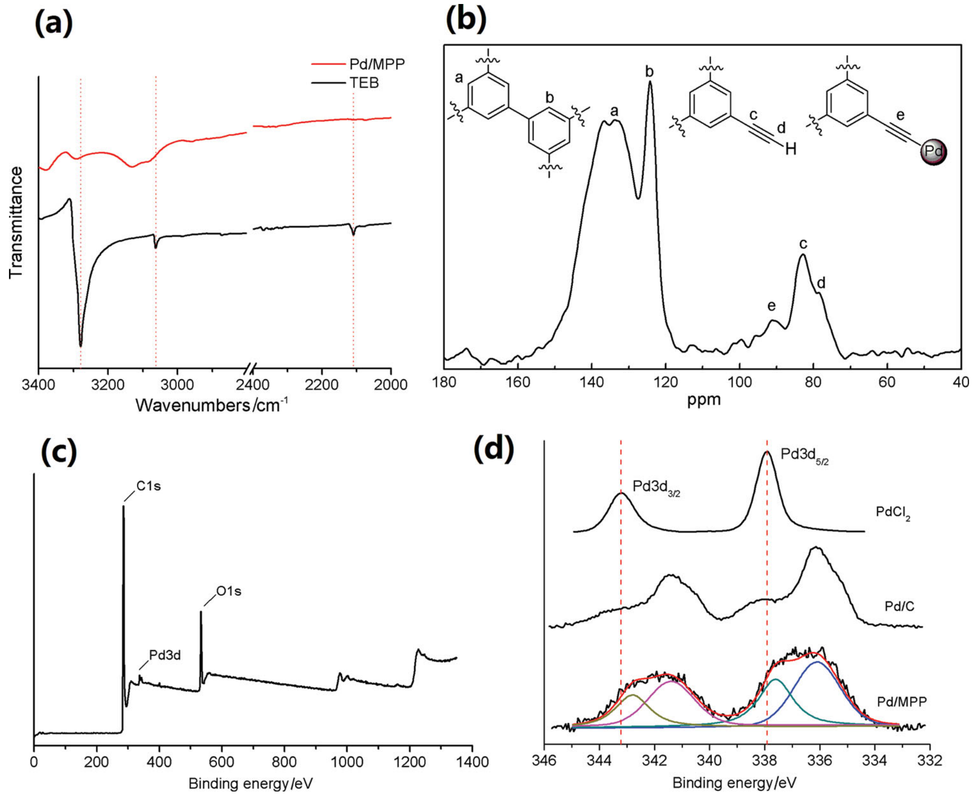

Figure 2. FT-IR spectra of Pd/MPP and TEB (a), the solid ^{13}C CP/MAS NMR result of Pd/MPP (b), XPS survey spectra of Pd/MPP (c), and XPS high-resolution spectra of Pd3d in $PdCl_2$, Pd/C and Pd/MPP (d).

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to the alkynyl groups are strongly attenuated. Meanwhile, the distinct peak corresponding to the aromatic hydrogen (3100 cm^{-1}) is significantly enhanced. These results indicate the successful alkynetrimerization and the formation of benzene rings, which are further supported by the solid-state ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR of Pd/MPP, as shown in Figure 2b. Signals at δ = 133.8 and 124.2 ppm are assigned to the different aromatic carbon atoms of the obtained MPP networks (marked 'a' and 'b' in Figure 2b).[32] The peak splitting at 133.8 ppm may attribute to the structural defects of the polyphenylene network. Interesting information comes from the other three peaks c, d, and e. Since the signal at 82.6 and 78.0 ppm corresponds to the alkynyl carbons connecting with phenyls and hydrogen atoms, respectively, the weak peak at 91.3 ppm can be reasonably assigned to carbon atoms on alkyne being bounded to Pd clusters,[33] demonstrating the presence of both terminal alkynyl groups and their covalent bonding to Pd clusters. X-ray photoelectron spectroscopy (XPS) investigation (Figure 2c and d) showed the $Pd3d_{5/2}$ signal of Pd/MPP is a broad peak at 336.6 eV as displayed in Figure 2d, which suggests the existence of both Pd(0) and Pd(II) in the product. Compared with the signals of $PdCl_2$ and commercial Pd/C, the broad peaks at 336.6 eV and 342.0 eV can reasonably been split into two sub-peaks: 336.1 eV and 334.4 eV, corresponding to $Pd3d_{5/2}$ and $Pd3d_{3/2}$ of Pd(0), respectively. Meanwhile the sub-peaks at 337.6 eV and 342.8 eV for $Pd3d_{5/2}$ and $Pd3d_{3/2}$ of Pd(II) are observed as well. It's also notable that the signals of Pd(II) are slightly shifted to lower binding energy (about 0.4 eV) in comparison with that of $PdCl_2$, which is mainly due to the relatively weak electron-withdrawing ability of terminal alkynes. Based on the XPS analysis, the contents of Pd(II) species of Pd in Pd/MPP is ca. 40.8%. These results disclose that some atoms of Pd clusters form covalent bonds with terminal alkynes just like silver acetylide or other reports about metal-alkynes,[34,35] while others still keep the state of zero-valence. These results further indicate that the produced Pd clusters are covalently stabilized by the untrimerizated alkynes distributed in the MPP networks.

The high resolution transmission electron microscopy (HR-TEM) image and the scanning transmission electron microscopy (STEM) image of typical Pd/MPP sample shows amorphous and highly porous structure in which the Pd clusters with an average diameter of 1.7 ± 0.2 nm are embedded and distributed homogeneously (**Figure 3**a and b). The powder X-ray diffraction (XRD) pattern of Pd/MPP (Figure S3) shows two broad bulges at a 2 Theta degree of 20 and 40, which can be assigned to amorphous MPP networks and the fine crystal particles of Pd(111), respectively. The calculated average particle size of Pd clusters using Scherrer formula is 1.8 nm, fitting well to the statistical results of HR-TEM characterizations.

Nitrogen adsorption desorption analysis (**Figure 4**) shows that Pd/MPP exhibits high surface areas of 659 m^2/g with a total pore volume of 0.35 cm^3/g, which are also the highest values reported in Pd@CMP materials. More importantly, the catalytic moieties are introduced in the synthesis step rather than via post treatment, so that the porous structures and the surface properties of MPP are reserved in a high level. Pore size distribution calculation (nonlocal density functional theory, NLDFT) demonstrates the existence of pores with a diameter of 0.7 nm, 1.2 nm, and a broad pore distribution in 1.2~5.0 nm, respectively (Figure 4). Compared with most of the reported CMPs, COFs, or MOFs with rather small pores of less than 2 nm, the Pd/MPP holds both micropores and mesopores which afford not only nanoreactors but diffusion channels,[36] providing an ideal platform as catalyst.

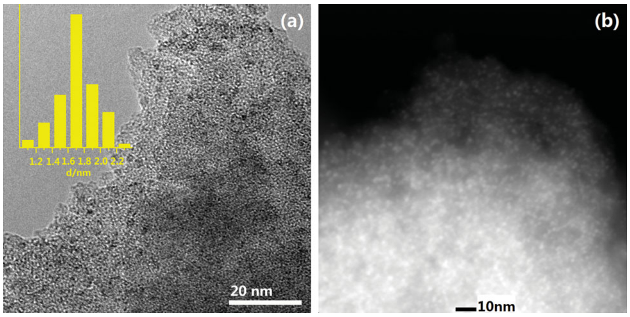

Figure 3. The HR-TEM images and particle size distributions for Pd/MPP (a) and STEM images of Pd/MPP (b).

It should be noted that the loading amount of Pd clusters in MPP, a critical issue for practical applications, can be feasibly adjusted by simply tuning the molar ratio of TEB and $Pd(PPh_3)_4$, without any significant effect on the Pd cluster size distributions (**Figure 5**), for which other previously reported methods are difficult to achieve.

2.3. Catalytic Activity tests of Pd/MPP

The catalytic activity of Pd/MPP is evaluated for catalyzing Suzuki–Miyaura coupling reactions. Surprisingly, the Pd/MPP catalyst shows very high catalytic activity for driving the

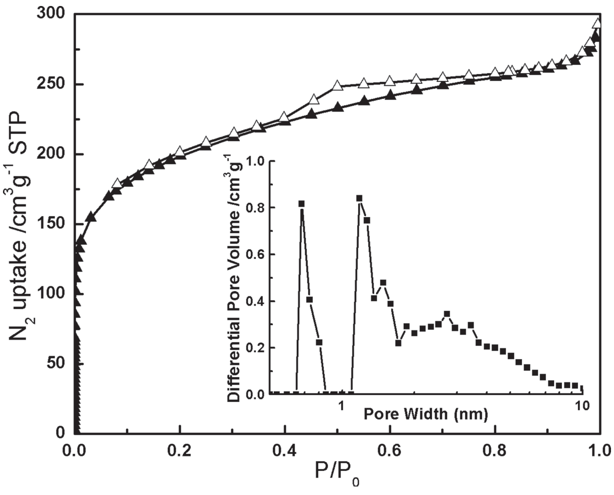

Figure 4. N_2 adsorption-desorption analysis and pore size distribution of Pd/MPP.

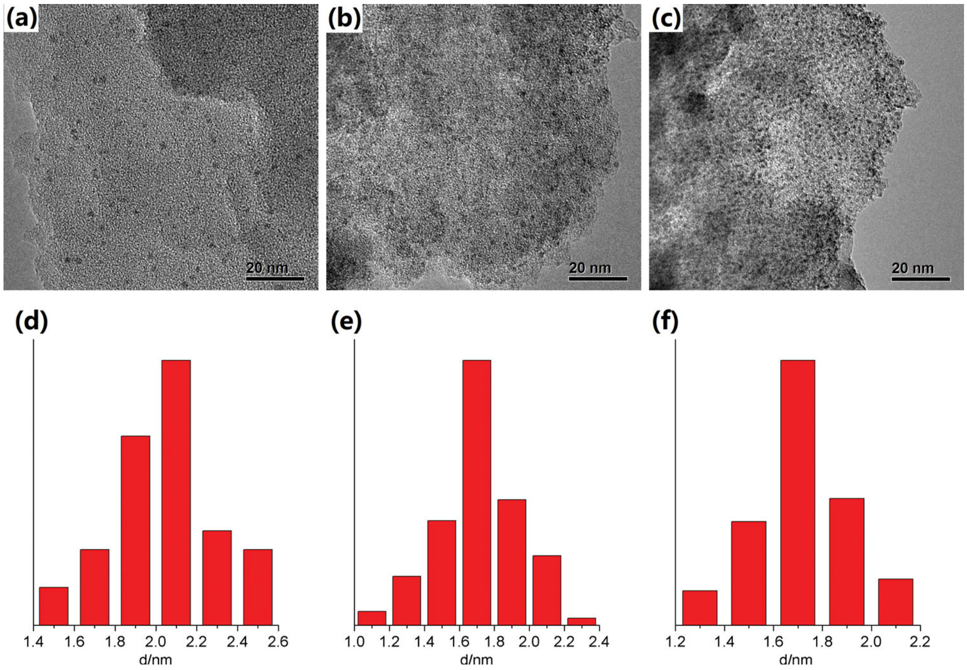

Figure 5. HR-TEM images and particle size distributions for Pd/MPP synthesized by different reactant ratio. The molar ratio for TEB and $Pd(PPh_3)_4$ was 20:1, 10:1, and 5:1 for (a), (b), and (c), respectively. It clearly shows different loading amount of Pd clusters (2.21 wt%, 4.56 wt% and 11.6 wt% for (a), (b), and (c), respectively, determined by ICP-OES analysis), but comparable particle size distributions: 2.0 ± 0.2 (d), 1.7 ± 0.2 (e) and 1.7 ± 0.2 (f) for (a), (b), and (c), respectively.

reaction even in aqueous media under aerobic conditions. As summarized in **Table 1**, using only 0.2 mol% of Pd/MPP catalyst, the coupling reaction of phenylboronic acid with substituted aryl bromides can be finished in short time (0.25–1 h) with excellent yield (95–99%) at 80 °C in air. In fact, some of the aryl bromides with an electron-withdrawing group can reach the end of the reaction in just a few minutes; and even 0.005 mol% of Pd/MPP is proved to be highly efficient for this reaction just as Table 1, **entry 8** shows. Taking 1 hour as the reasonable reaction time, both the calculated turnover number (TON, 1.92×10^4) and the turnover frequency (TOF, 1.92×10^4 h^{-1}) are at a high level while maintaining a good yield, for which other frequently used catalysts are difficult to achieve. It is worthwhile noted that either electron-donating or electron-withdrawing substituent of aryl bromides has little influence on the catalysis, and no by-product such as the formation of homo-coupling products from aryl bromides or phenylboronic acid has been detected in the reaction. Meanwhile, we also compare the activity of Pd/MPP with previously reported results (Table S1 in the Supporting Information). Very high yield of the selected reaction has been achieved on Pd/MPP with much shorter reaction time even in air, indicating the excellent catalytic performance of Pd/MPP.

However, the Suzuki reactions for aryl chlorides can only gave unsatisfied yield under similar conditions; the cross-coupling between phenylboronic acid and p-chloroacetophenone gives less than 30% yield even after 24 h. (Table 1, **entry 9**) This may due to that the activation of aryl chlorides is much more difficult than aryl bromides and always requires harsher reaction conditions in heterogeneous catalysis system; and better results may be achieved by adjusting the reaction conditions and processed under inert atmosphere.

As heterogeneous catalyst, Pd/MPP is feasible to be dispersed in organic solvents, and is amenable to facile filter separation and recycling. Recycle tests of Pd/MPP demonstrate that its catalytic activity and selectivity do not decrease even after 5 cycles (Table 1, **entry 10**). HR-TEM characterizations demonstrate that the Pd clusters still hold quite small diameters of 3.5 ± 1.5 nm with relatively narrow (1–5 nm) particle size distribution even after 5 cycles (**Figure 6**a). Statistic evaluation shows that a large number of particles are still smaller than 3.5 nm which are believed to be highly active for catalysis reactions (Figure 6b). We also perform XPS analysis on Pd/MPP after 5 cycles and compare the results with the XPS spectra of fresh Pd/MPP, just as Figure S5 shows. After 5 cycles, the Pd(II) contents of Pd in Pd/MPP is dropped to 22.9% accroding to XPS results, while the catalytic activity of Pd/MPP is still very high. Combined with the HR-TEM characterizations, it is indicating that Pd nanoparticles are slightly grown up but still been covalently bonded to the support even after 5 cycles. Meanwhile, the liquid phase of the reaction mixture was collected by hot filtration after each cycle. Only very low amount of dissolved palladium (less than 0.2% of the total palladium) is detected in the liquid by inductively coupled plasma optical emission spectrometer (ICP-OES), which shows no catalysis activity for a new reaction. Obviously, the excellent stability and high activity of Pd/MPP is in close relation to its unique structure where Pd clusters is covalently stabilized and semi-embedded in the three-dimensional network of MPP.

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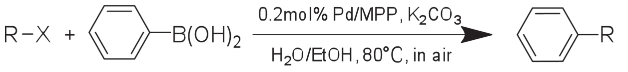
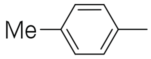
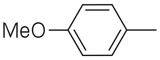
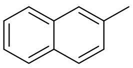
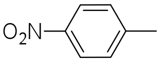
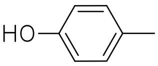
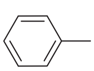
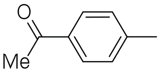
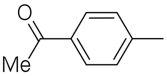
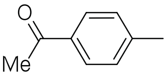
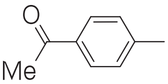
Table 1. Catalytic activity test of Pd/MPP for Suzuki–Miyaura coupling reactions.



Entry	R	X	Time [h]	Yield [%][a)]
1		Br	0.5	98
2		Br	1	97
3		Br	0.75	99
4		Br	0.5	96
5		Br	1	95
6		Br	0.5	96
7		Br	<0.25	98
8[b)]		Br	1	96
9		Cl	24	<30
10[c)]		Br	<0.25	98

[a)]Isolated yield; [b)]0.005 mol% Pd/MPP was used; [c)]After 5 cycles.

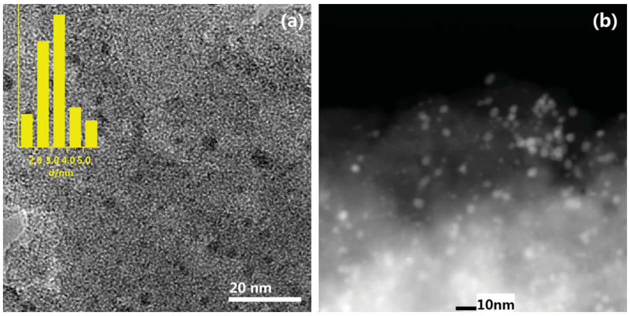


Figure 6. The HR-TEM images and particle size distributions for Pd/MPP after 5 cycles (a) and STEM images of Pd/MPP after 5 cycles (b).

3. Conclusion

In summary, a novel and high efficient catalyst Pd/MPP for Suzuki–Miyaura coupling reaction has been synthesized with an in-situ one-pot chemical approach via catalytic trimerization of TEB. The unique Pd/MPP exhibits not only high surface area, gradient pore size distribution, and monodispersed and highly stabilized Pd clusters, but very high catalytic activity for a broad scope of Suzuki–Miyaura reactions in aqueous media under aerobic conditions with short reaction time, good yield, and high TON and TOF values. The strong covalent interaction between Pd and MPP network prevents the agglomeration or leaching of Pd clusters and enable the Pd/MPP catalyst to remain highly active even after a number of cycles. This work opens up a new window for developing various MPP-based catalysts, in which the MPP can act as a stable, robust, and versatile stabilizer to host not only Pd but other noble metal clusters for catalyzing a wide scope of reactions with high efficiency.

4. Experimental Section

Typical procedure for Pd/MPP: TEB (150 mg, 1 mmol) and Pd(PPh_3)$_4$ (115.5 mg, 0.1 mmol) were dissolved in THF (5.0 mL) and kept stirring for 12 h at 65 °C under reflux at ambient atmosphere. The obtained solid was washed with THF, dichloromethane and ethanol repeatedly. Further purification was carried out by Soxhlet extraction from dichloromethane, and then dried at 80 °C under vacuum to yield Pd/MPP as a brown powder almost quantitatively. The Pd content was 4.56 wt% as determined by ICP-OES analysis.

Catalytic Tests: These were carried out in a reaction tube sealed with a Teflon screw cap. The tube was charged with boronic acid (0.6 mmol, 1.2 equiv), sodium carbonate (106 mg, 1 mmol, and 2 equiv), aryl bromide or aryl chloride (0.5 mmol, 1 equiv), Pd/MPP (0.2 mol% Pd based on arylbromide), ethanol (2 mL) and water (2 mL). The flask was sealed with air and stirred in a preheated oil bath (80 °C) until reaction finished (monitored by TLC). After cooling down to room temperature, the product was extracted into dichloromethane and washed with water to remove potassium carbonate. After further purification by column chromatography over silica gel and removing the solvent under reduced pressure, the desired products were obtained. In recycle tests, the catalyst was washed with water and dried, and then used again directly after each cycle.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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