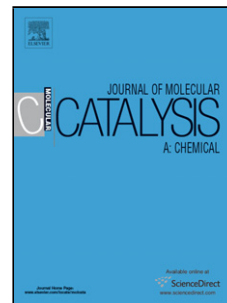## Accepted Manuscript

Title: Palladium nanoparticles supported on graphene and reduced graphene oxide as efficient recyclable catalyst for the Suzuki-Miyaura reaction of potassium aryltrifluoroborates

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Dedicated to the memory of Prof. Carlos F. Barbas III

Palladium nanoparticles supported on graphene and reduced graphene oxide as efficient recyclable catalyst for the Suzuki-Miyaura reaction of potassium aryltrifluoroborates

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Highlights

Palladium nanoparticles supported on Graphene efficiently catalyze Suzuki reaction.
Catalyst can be easily recycled, especially using microwave irradiation.
Coupling reaction can be scaled up to multi-gram scale.
Catalyst stability is higher under microwave irradiation than conventional heating.
Nanoparticles dissolution/re-deposition mechanism is involved.

Abstract:

Palladium nanoparticles supported in graphene platelets have been efficiently used as catalyst in the Suzuki-Miyaura coupling between aryl bromides and potassium aryltrifluoroborates using 0.1 mol% of Pd and potassium carbonate as base in MeOH/H_2O as solvent at 80 ºC. The reaction can be performed using conventional and microwave heating showing the catalyst high reusability, particularly with microwaves, where lower aggregation of Pd nanoparticles has been observed. A dissolution/re-deposition catalytic mechanism is proposed, based on the fact that palladium leaching to the solution is detected under microwave irradiation.

Keywords: Graphene / Reduced graphene oxide / Suzuki / Palladium / Supported Catalysis

1. Introduction

During the past few years, graphene (G) has attracted immense interest in basic materials science and device applications due to its extraordinary thermal, mechanical, and electrical properties [1]. With a unique 2D sp^2 hybrid carbon network, an excellent chemical stability, and a high surface area, graphene-based architectures are highly desirable in nanocomposite materials[2] and especially as a support for metal nanoparticles[3]. Furthermore, graphene derivatives[4], such as graphene oxide (GO)[5], and reduced graphene oxide (rGO)[6], have been also shown as useful supports in catalysis

since their structural defects allow surface functionalization, enhancing the interactions with the anchored metal nanoparticles[7].The palladium-catalyzed Suzuki-Miyaura cross-coupling reaction has become one of the most useful tools to construct carbon-carbon bonds in both laboratory and industry[8]. Although many of the catalytic systems for the Suzuki reaction have been developed and used under homogeneous conditions, much effort has been recently directed to the search for alternative heterogeneous analogous palladium catalysts[9], in order to avoid product contamination and facilitate the recycling and reuse of the catalysts. While some heterogeneous palladium catalysts have provided comparable activities and efficiencies on a par with their homogeneous counterparts in the Suzuki reaction, this is not a general behavior, and lots of work has yet to be done to improve the performance of heterogeneous systems [10]. Therefore, highly active and easily separable and reusable palladium catalysts are considered an important objective for Suzuki coupling reactions. Palladium nanoparticles (PdNPs)[11] have been established as a promising alternative in the search for highly active ligand-free catalysts due to their high surface-to-volume ratio and their highly active surface atoms compared to those of the bulk catalysts. The use of PdNPs reduces costs, simplifies workup procedures, facilitates the separation of the final product, and allows recycling and continuous processing, especially when they are immobilized in a solid support[12]. Palladium nanoparticles supported on graphene and graphene derivatives increase the surface area of the composite, enlarging the distance between the sheets. This phenomenon improves the catalytic activity of this type of heterogeneous catalysts, as recently demonstrated in the Suzuki-Miyaura reaction, which by far, has been the most studied cross-coupling process using different graphene derivatives as palladium nanoparticles supports. Among them, graphene[13], graphene oxide[14], reduced[15] or partially reduced graphene oxide[16], and functionalized graphene[17] and graphene oxide[18] have been successfully used in the palladium-catalyzed Suzuki-Miyaura coupling between aryl iodides, bromides, and activated chlorides with arylboronic acids. However, to the best of our knowledge, no studies have been performed involving other boron-derived nucleophiles[19] such as potassium aryltrifluoroborates[20] or boronic acid esters[21].

Herein, as part of our interest in palladium-catalyzed Suzuki-Miyaura reactions using highly active catalysts[22],we present the study of immobilized palladium nanoparticles on graphene nanoplatelets(PdNPs-G) and reduced graphene oxide (PdNPs-rGO) as catalyst in the Suzuki-Miyaura coupling of potassium aryltrifluoroborates with aryl halides. Three different catalysts **1**-**3**have been evaluated in this study (Figure 1).

2. Experimental

Unless otherwise noted, all commercial reagents and solvents were used without further purification. Melting points were determined with a Reichert Thermovar hot plate apparatus and are uncorrected. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were obtained on a Bruker AC-300, using $CDCl_3$ as solvent and TMS as reference, unless otherwise stated. Low-resolution electron impact (EI) mass spectra were obtained at 70 eV on an Agilent 5973 Network Mass selective detector. Analytical TLC was performed on Merck aluminum sheets with silica gel 60 F_{254}. Silica gel 60 (0.04-0.06 mm) was employed for flash chromatography. Microwave reactions were performed on a CEM Discover Synthesis Unit (CEM Corp., Matthews, NC) with a continuous focused microwave power delivery system in glass vessels (10 mL) sealed with a septum under magnetic stirring. The temperature of the reaction mixture inside the vessel was monitored using a calibrated infrared temperature control under the reaction vessel. The conversion of the reactions was determined by GC analysis on an Agilent 6890N Network GC system. Centrifugations were carried out in a Digicen centrifuge (OrtoAlresa, 2000 rpm, 20 minutes).TEM analyses were carried out in a JEOLJEM-2010 apparatus equipped with a Gatan acquisition camera. The size distribution of the palladium nanoparticles was determined by measuring the particle diameter using Image J 1.49b software

on the images obtained by TEM. ICP-MS were performed on an Agilent 7700x equipped with HMI (high matrix introduction) and He mode ORS as standard. Catalysts **1-3** are commercially available and have been obtained from NanoInnova Technologies S. L.

2.1. Typical procedure for the Suzuki-Miyaura coupling reaction under conventional heating conditions

A 10 mL glass vessel was charged with catalyst **2** (0.3mg, 0.1 mol% Pd), 4-bromoanisole (21 μL, 0.16 mmol, 1 eq), potassium phenyltrifluoroborate (38 mg, 0.20 mmol, 1.25 eq), K_2CO_3 (45.5 mg, 0.33 mmol, 2 eq) and $MeOH/H_2O$: 3/1 (0.4 mL).The vessel was sealed with a pressure cap, and the mixture was stirred and heated at 80 ^{o}C for 20 h. Then, the mixture was cooled at room temperature and H_2O (4 mL) and EtOAc (4 mL) were added. The mixture was filtered with cotton and extracted with EtOAc (3 × 10 mL). The organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by flash chromatography (silica gel, hexane/EtOAc: 6/1) to obtain 0.0275g of pure compound **4** (94% yield).

2.2. Typical procedure for the Suzuki-Miyaura coupling reaction under MW irradiation conditions

A 10 mL MW vessel was charged with catalyst **2** (0.3 mg, 0.1 mol% Pd), 4-bromoanisole (21 μL, 0.16 mmol, 1 eq), potassium phenyltrifluoroborate (38 mg, 0.20 mmol, 1.25 eq), K_2CO_3 (45.5 mg, 0.33 mmol, 2 eq) and $MeOH/H_2O$: 3/1 (0.4 mL). The vessel was sealed with a pressure cap and the mixture was heated at 80 ^{o}C using MW irradiation (initial irradiation power 40 W) for 2 h in a CEM Discover MW reactor. The mixture was cooled at room temperature and H_2O (4 mL) and EtOAc (4 mL) were added. The mixture was filtered with cotton and extracted with EtOAc (3 × 10 mL). The organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by flash chromatography (silica gel, hexane/EtOAc: 6/1) to obtain 0.0269 g of pure compound **4** (92% yield).

2.3. Typical procedure for catalyst recovery

Once the reaction was finished, the mixture was diluted with 10 mL of a mixture of $EtOAc/MeOH/H_2O$: 4/3/1 (volume ratio) and stirred. This mixture was centrifuged (2000 rpm, 20 minutes) and the solvent was subtracted using a syringe with a syringe filter (4 mm PTFE syringe filter, 0.2 μm). The washing/centrifugation sequence was repeated four additional times until no product was detected in the liquid phase by thin layer chromatography. The residual solvent was completely removed under reduced pressure affording the Pd catalyst which was directly used in the same tube with fresh reagents for the next run. This procedure was repeated for every cycle and the conversion of the reaction was determined by GC chromatography using decane as internal standard.

3. Results and discussion

3.1. Catalysts activity and reaction conditions

Catalyst **1** (PdNPs-rGO/ODA) is a reduced graphene oxide, functionalized with octadecylamine (ODA, 0.1 mmol/g), where Pd(0) nanoparticles of 13 nm of average size (6% of Pd w/w) have been immobilized (Figure 1). The amino

functional group in the catalyst provides this catalyst with higher dispersion ability in organic solvents. The heterogeneous catalyst **2** contains 6% in weight of palladium(0) nanoparticles, with an average size of 5 nm, over a graphene support (PdNPs-G), while, in catalyst **3**, the palladium(0) nanoparticles (6.9 nm average size, 6% weight of Pd) are supported over a reduced graphene oxide (PdNPs-rGO) (Figure 1). Catalysts **2** and **3** disperse better in aqueous solvents.

The coupling between 4-bromoanisole and potassium trifluoroborate was selected as model reaction in order to study the catalytic activity of the palladium supported catalysts **1**-**3** (Scheme 1). We considered different parameters, such as the type and the amount of supported catalyst (i.e. **1**-**3**), and the solvent.

Initially, a mixture 1/1 MeOH/H$_2$O (substrate: 0.4 M) was used in the coupling reaction of 4-bromoanisole and PhBF$_3$K (1.25 equiv.) catalyzed by **1**-**3** (0.1 mol-% in Pd) in the presence of K$_2$CO$_3$ as base (2 equiv.), at 80 ºC during 20 h. Catalyst **1**, which scatters poorly in aqueous solvents, resulted totally inactive in this aqueous mixture (Table 1, entry 1). Unexpectedly, catalyst **1** also failed when the reaction was performed in an apolar solvent, such as toluene (Table 1, entry 2). A possible reason for the observed inactivity of catalyst **1** is the average size of the palladium nanoparticles which is higher (13 nm) than for catalysts **2** and **3**. Consequently, this amino-functionalized reduced graphene oxide was excluded from the following optimization assays.

In sharp contrast, catalysts **2** and **3**, in a 1/1 MeOH/H$_2$O mixture, gave 4-methoxybiphenyl (**4**) within 70 and 75% yield, respectively (Table 1, entries 3 and 4). The activity of both catalyst **2** and **3** decreased when the reactions were carried out in pure water or in pure methanol, giving **4** with lower yields than 46% in all cases (Table 1, entries 5-8). The use of three different surfactants was tested in order to improve the results of the reaction in water. Thus, the model reaction was performed employing catalyst **2** (0.1 mol-%) in the presence of 20 mol-% of each additive, α-tocopherylpolyoxyethanylsebacate (PTS, non-ionic additive), tetra-*n*-butylammonium bromide (TBAB, cationic surfactant), and sodium dodecylbenzenesulfonate (SDBS, anionic surfactant)(Table 1, entries 9-11). Only in the presence of SDBS an improvement in the formation of the coupling product was observed, reaching 49% yield (entry 11).

Considering the significant differences observed between the reactions carried out in a mixture methanol-water or in the pure solvents separately, two additional mixtures (1/3 and 3/1) of these solvents were tested, under the same reaction conditions, using catalysts **2** and **3**. The mixture MeOH/H$_2$O: 3/1 provided better results (Table 1, entries 12 and 14) for both catalysts. Moreover, under this new solvent system, the catalyst loading could be reduced to 0.01 mol-% with only an insignificant loss of activity (Table 1, entries 16 and 17). Additionally, when the reaction was performed under microwave irradiation (80 ºC, using an initial power of 40 W), the product was obtained in 92% yield (Table 1, entry 12, footnote d). Last, other palladium(0) sources, such as the heterogeneous Pd on carbon (Pd-C) and the homogeneous Pd$_2$(dba)$_3$, were employed. Lower yields were observed in both cases, particularly under homogeneous conditions (Table 1, entries 18 and 19). As a result of this optimization process, we concluded that the best reaction conditions to couple 4-bromoanisole and potassium phenyltrifluoroborate in aqueous media (mixture MeOH/H$_2$O: 3/1) involve the use of palladium nanoparticles over a graphene support (catalyst **2**, 0.1 mol-% on Pd) in the presence of potassium carbonate, at 80 ºC during 20 h.

Under these reactionconditions, product **4** was quantitative produced and isolated in 94% yield (Table 2, entry 1). Furthermore, in order to demonstrate the synthetic utility of the catalytic methodology, a multi-gram scale experiment was carried out. The reaction between 4-bromoanisole (0.0535 mol, 10 gr, 1 eq) and potassium phenyltrifluoroborate (0.0667 mol, 12.27 gr, 1.25 eq) catalyzed by **2** (0.1 mol-% Pd) under conventional heating conditions (80 ºC), provided product **4**with a 99% isolated yield.

3.2. Catalyst stability and recyclability

One of the most important advantages of heterogeneous nanoparticle catalysts are their recovery and recyclability. Thus, a study of catalyst **2** recyclability was carried out on the model reaction, i.e. the coupling between 4-bromoanisole and potassium phenyltrifluoroborate using 1 mol-% of palladium catalyst **2**[23]under conventional and microwave heating (Scheme 2). After each cycle, the catalyst was easily separated from the reaction mixture by washing the crude reaction with a solvent mixture (EtOAc/MeOH/H$_2$O) and subsequent centrifugation (see SI, for details). As depicted in Scheme 2, catalyst **2** can be easily recycled at least eight times without losing the catalytic activity when using microwave irradiation conditions. However, under conventional heating reaction conditions, the activity of catalyst **2** significantly dropped after five runs. Inductively coupled plasma mass spectrometry (ICP-MS) analysis of the washings[24] after the first run under both reaction conditions (MW and conventional heating) showed different Pd leaching levels for catalyst **2**. Thus, while 1103 ppb of Pd leached from **2** under microwave irradiation conditions, only 15 ppb of Pd were detected on the washings after the first cycle using conventional heating. Therefore, the leaching of palladium nanoparticles from **2** should not be the main reason for the observed decreased catalytic activity after 5 runs under conventional thermal conditions. Then, transmission electron microscopy (TEM) analysis of catalyst **2** was performed (Figure 3) and the nanoparticle size distribution was determined after 8 cycles using conventional and microwave heating. Although the agglomeration of Pd nanoparticles on the graphene sheets was insignificant in both cases (Figure 3), we observed that the average nanoparticle size for catalyst **2** (originally 4.5 nm), after 8 runs, had increased much more using conventional heating compared to microwave heating (13.4 nm *versus* 6.6 nm). This could justify the lower reactivity of the recycled catalyst **2** after being used under conventional heating reaction conditions.

In order to gain insight into the homogeneous or heterogeneous behaviour [26] of catalyst **2** using conventional heating conditions, a hot filtration experiment[25] was carried out (see SI). Then, under the optimized reaction conditions (catalyst **2**, 0.1 mol% Pd), the reaction coupling between of 1-bromo-4-methoxybenzene and potassium phenyltrifluoroborate was carried out for 3 h. After this time an ~8% conversion of the Suzuki coupling was observed by GC analysis. Then, the catalyst was removed by centrifugation and the obtained filtrates were transferred to another reaction flask where stirring continued at 80 ºC. After 17 h, no reaction progress was observed (GC analysis showed 8% conversion). On the other hand, a second hot filtration experiment was carried out where no centrifugation was performed to prevent that leached Pd re-deposits on the catalyst support. In this case, a slight increase of the reaction conversion (8% to 15%) was observed after 17 h. This experiment was in agreement with the low Pd leaching observed by ICP-MS from the solid support using conventional heating, as described above.

The homogeneous/heterogeneous behaviour of catalyst **2** under microwave irradiation reaction conditions was also studied. A hot filtration experiment performed with only the catalyst (see SI for details) clearly confirmed the coexistence of a dissolution/re-deposition mechanism [27].Thus, after heating (MW, 80 ºC) for 15 minutes catalyst **2** (0.1 mol% Pd) in a MeOH/H$_2$O: 3/1 mixture, the filtrate was monitored for continued activity after adding fresh reactants, observing only a 2% conversion after 1 h and 45 min when the catalyst was separated by centrifugation (the active Pd was re-deposited on the solid support), and a 99% conversion when the filtrate was separated from the catalyst without centrifugation.

3.3. Catalyst scope

Next, different electrophiles were employed under the optimized conditions, to study the scope of the reaction using catalyst **2** (Table 2). Potassium phenyltrifluoroborate reacted with the deactivated and sterically hindered 2-bromotoluene producing the corresponding biaryl **5** in 45% isolated yield, albeit the conversion was 78% (Table 2, entry 2).Sterically hindered electrophiles, like 2-bromo-1,3-dimethylbenzene, were unsuccessful in the cross-coupling reaction with potassium phenyltrifluoroborate (Table 2, entry 3). On the contrary, activated aryl bromides (i.e. 4-bromoacetophenone) and 1-bromonaphthalene, produced the corresponding biarylic systems **7** and **8** within 74% and 64% isolated yield, respectively (Table 2, entries 4 and 5). Furthermore, heterocyclic bromides, such as 2-bromopyridine and 2-bromothiophene, were coupled with potassium phenyltrifluoroborate, producing compounds **9** and **10** with low yields (Table 2, entries 6 and 7), which could be slightly improved by increasing both the catalyst loading to 1 mol-% and the amount of nucleophile to 2 equiv (Table 2, entries 6 and 7, footnote b).

The use of more reactive electrophiles (i.e. 4-iodoanisole, phenyl triflate and 4-methoxyphenyldiazonium tetrafluoroborate), under the optimized reaction conditions for aryl bromides, gave very different results. For example, 4-iodoanisole coupled effectively with potassium phenyltrifluoroborate giving product **4** with 96% yield (Table 2, entry 8). However, phenyl triflate only produced the expected product **11** in 14% yield and the diazonium salt did not yield any cross-coupling product (Table 2, entries 9 and 10). Last, the reactivity of aryl chlorides was tested employing the activated 4-chloroacetophenone, but the corresponding biphenyl **7** was only obtained with 7% yield under the optimized reaction conditions for aryl bromides (Table 2, entry 11).

The nucleophiles scope was also sutied by employing different potassium aryl- and heteroaryltrifluoroborates, as well as other boron-derived reagents (Table 3). Initially, potassium 2- and 4-tolyltrifluoroborate were effectively coupled with 4-bromoanisole, yielding the corresponding biaryls **12** and **13** with 72% and 68% respectively (Table 3, entries 1 and 2). Furthermore, 1-bromo-2-methylbenzene yielded product **14** in62% by reaction with potassium 4-methylphenyltrifluoroborate, although it was only isolated with a 62% yield due to its volatility (Table 3, entry 3). The more deactivated nucleophile potassium 4-(trifluoromethyl)phenyltrifluoroborate gave lower yield in the coupling with 4-bromoanisole (Table 3, entry 4). Regarding the use of heterocyclic trifluoroborates,the reaction between 4-bromoacetophenone and potassium 2-thienyltrifluoroborate gave product **16** in 50% yield, although 1 mol-% Pd and 2 equivalents of nucleophile were necessary (Table 3, entry 5). Concerning other boron reagents, phenylboronic acid resulted slightly less active than the corresponding trifluoroborate (Table 3, entry 6); the reactivity of the pinacol boronate was even lower (Table 3, entry 7), and the *N*-methyliminodiacetic acid (MIDA) derivative lacked completely of reactivity under the employed reaction conditions (Table 3, entry 8).

4. Conclusions

To conclude, we have employed palladium nanoparticles supported over graphene (G) and reduced graphene-oxide (rGO) as readily efficient catalysts in the Suzuki-Miyaura coupling between aryl bromides and potassium aryltrifluoroborates. Both catalysts, **2** (Pd-G) and **3** (Pd-rGO), which disperse properly in aqueous media, resulted very active for this process in a mixture $MeOH/H_2O$, being the solvent ratio an essential parameter (best results for ratio $MeOH/H_2O$: 3/1). Both conventional heating and microwave irradiation provided similar results for the coupling reaction. Catalyst **2** can be recovered by centrifugation and recycled without any loss of activity, up to 8 times for reactions carried out under

==microwave irradiation==, or 4 times ==when== conventional heating ==is the methodology employed==. The higher agglomeration ==of Pd nanoparticles== observed under conventional heating ==conditions== seems to be the reason for the deactivation ==of catalyst **2**==. Furthermore, we have proved that the palladium leached during the reaction is mostly re-deposited on the solid support after the reaction, ==being this recovery process favored by centrifugation.==Finally, the reaction can be scale-up to multi-gram scale without any loss of catalyst activity.

Acknowledgements

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[23] Since small scale reactions have been performed throughout this study (see SI), the recycling experiments were performed using 1 mol% Pd in order to facilitate the catalyst recovery.

[24] To perform these studies, the catalyst was separated and recovered from the reaction mixture without centrifugation in order to minimize a possible re-deposition of the leached Pd species back on the support. Then, the samples for ICP analysis were taken from the crude reaction mixture after 15 minutes without stirring.

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Scheme 1. Model Suzuki-Miyaura reaction catalyzed by catalyst 1-3.

Scheme 2. Catalyst 2 recyclability and yields in the Suzuki-Miyaura coupling in different cycles.

Figure 1. Palladium(0) supported catalysts employed in this study.

Figure 2. TEM images of catalyst **2** after 8 reaction cycles using conventional (**a**, 10 nm; **b**, 20 nm) and microwave heating (**c**, 10 nm; **d**, 20 nm).

Figure 3. a) Size distribution of Pd nanoparticles for catalyst **2**. b) Size distribution of Pd nanoparticles for catalyst **2** after 8 cycles using conventional heating conditions. c) Size distribution of Pd nanoparticles for catalyst **2** after 8 cycles using microwave heating conditions. Min Mean, Max and Mode refer to the corresponding statistical values for the size distribution of the Pd nanoparticles.

Table 1. Reaction conditions study. Catalyst and solvent.[a]
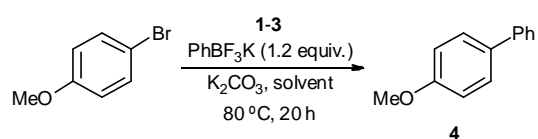
Entry	Cat. (% Pd)	Solvent	Additive[b]	Yield (%)[c]
1	**1** (0.1)	MeOH/H_2O: 1/1	---	<5
2	**1** (0.1)	Toluene	---	<5
3	**2** (0.1)	MeOH/H_2O: 1/1	---	70
4	**3** (0.1)	MeOH/H_2O: 1/1	---	75
5	**2** (0.1)	H_2O	---	26
6	**3** (0.1)	H_2O	---	25
7	**2** (0.1)	MeOH	---	46
8	**3** (0.1)	MeOH	---	24
9	**2** (0.1)	H_2O	TBAB	28
10	**2** (0.1)	H_2O	PTS	22
11	**2** (0.1)	H_2O	SDBS	49
12	**2** (0.1)	MeOH/H_2O: 3/1	---	>99 (92)[d]
13	**2** (0.1)	MeOH/H_2O: 1/3	---	43
14	**3** (0.1)	MeOH/H_2O: 3/1	---	87
15	**3** (0.1)	MeOH/H_2O: 1/3	---	46
16	**2** (0.05)	ΜCEOH/H_2O: 3/1	---	87
17	**2** (0.01)	MeOH/H_2O: 3/1	---	82
18	Pd-C (0.1)	MeOH/H_2O: 3/1	---	73
19	Pd$_2$(dba)$_3$ (0.1)	MeOH/H_2O: 3/1	---	14

[a] Reaction conditions: 4-bromoanisole (0.16 mmol), PhBF$_3$K (0.20 mmol), **1-3** (0.1 mol-%), K$_2$CO$_3$ (0.33 mmol), solvent (0.4 mL), at 80 ºC during 20 h.
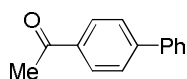
[b] Surfactant was employed in 20 mol-%.

[c] Yield of coupling product **4** determined by GC using decane as internal standard.

[d] In brackets, reaction performed under microwave irradiation at 80 ºC (initial power: 40 W) during 2 h.

Table 2. Substrate scope: Electrophiles.

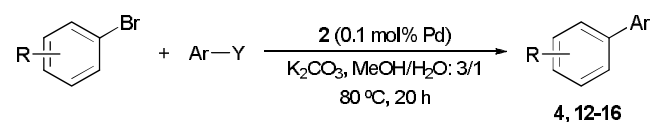| Entry	Ar–X	Product	No.	Yield (%)[a]
1	4-MeOC$_6$H$_4$Br	MeO—⟨ ⟩—Ph	**4**	94
2	2-MeC$_6$H$_4$Br	⟨ ⟩—Ph / Me	**5**	45 (78)
3	1,3-(Me)$_2$C$_6$H$_3$-2-Br	Me / ⟨ ⟩—Ph / Me	**6**	< 5
4	4-MeCOC$_6$H$_4$Br	Me-CO—⟨ ⟩—Ph	**7**	74
5	1-Br-naphthalene	naphthalene-Ph	**8**	64
6	2-Br-pyridine	⟨N⟩—Ph	**9**	15 (21)[b]
7	2-Br-thiophene	⟨S⟩—Ph	**10**	39 (64)[b]
8	4-MeOC$_6$H$_4$I	MeO—⟨ ⟩—Ph	**4**	96
9	4-MeOC$_6$H$_4$N$_2$BF$_4$	MeO—⟨ ⟩—Ph	**4**	< 5
10	PhOTf	⟨ ⟩—Ph	**11**	14

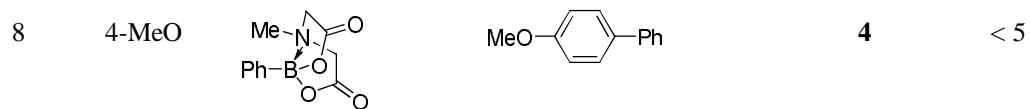| 11 | 4-MeCOC$_6$H$_4$Cl | | **7** | 7 |

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[a] Pure product isolated yield after purification by column chromatography. In brackets, conversion determined by GC.

[b] Catalyst **2** loading was 1 mol-%, together with 2 equiv. of nucleophile.

Table 3. Substrate study: Potassium aryltrifluoroborates and other boron reagents.
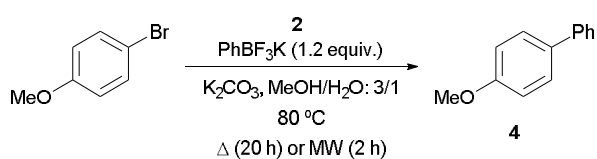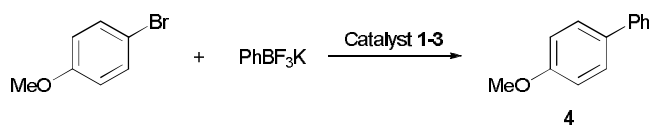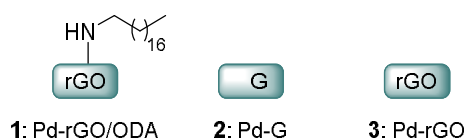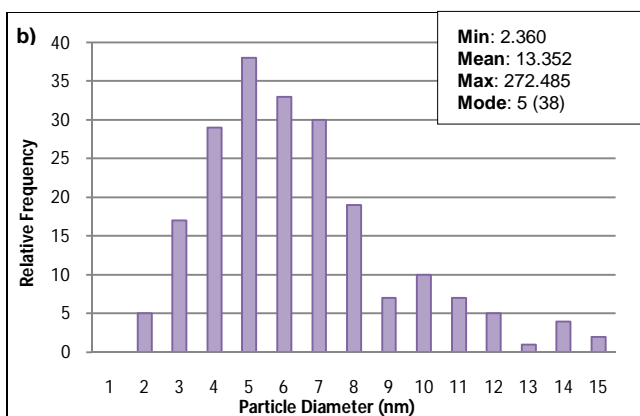

Entry	R^1	Ar–Y	Product	**No.**	Yield (%)^a
1	4-MeO	2-MeC$_6$H$_4$BF$_3$K		**12**	72
2	4-MeO	4-MeC$_6$H$_4$BF$_3$K		**13**	68
3	2-Me	4-MeC$_6$H$_4$BF$_3$K		**14**	62 (68)
4	4-MeO	4-(CF$_3$)C$_6$H$_4$BF$_3$K		**15**	35
5	4-MeCO	(2-Thienyl)BF$_3$K		**16**	50^b
6	4-MeO	PhB(OH)$_2$		**4**	90
7	4-MeO			**4**	73

| 8 | 4-MeO | | MeO—Ph | **4** | < 5 |

MeO—(Br) + PhBF$_3$K $\xrightarrow{\text{Catalyst } \mathbf{1\text{-}3}}$ MeO—(Ph) **4**

MeO—(Br) $\xrightarrow[\substack{\text{K}_2\text{CO}_3,\ \text{MeOH/H}_2\text{O: 3/1} \\ 80\ ^\circ\text{C} \\ \Delta\ (20\ \text{h})\ \text{or MW (2 h)}}]{\substack{\mathbf{2} \\ \text{PhBF}_3\text{K (1.2 equiv.)}}}$ MeO—(Ph) **4**

Run	1	2	3	4	5	6	7	8
MW Yield (%)	>99	>99	>99	>99	91	95	97	>99
Δ Yield(%)	>99	>99	>99	90	83	58	44	40

1: Pd-rGO/ODA   **2**: Pd-G   **3**: Pd-rGO

a)

Min: 2.095
Mean: 4.495
Max: 11.718
Mode: 5.750 (84)

b)

Min: 2.360
Mean: 13.352
Max: 272.485
Mode: 5 (38)
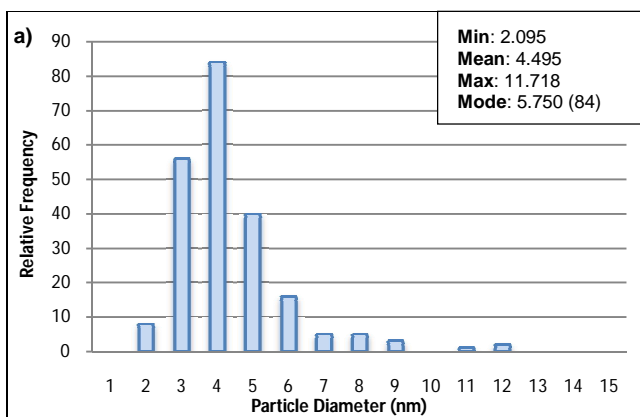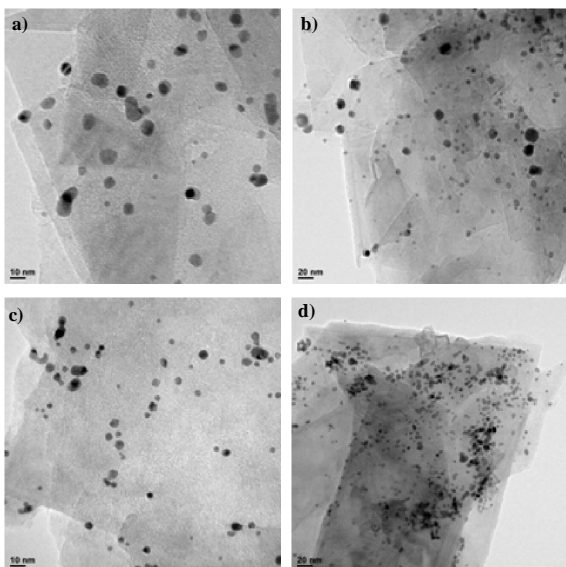
Min: 2.394
Mean: 6.594
Max: 19
Mode: 3.789 (43)