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Oxygen-promoted coupling of arylboronic acids with olefins catalyzed by $[CA]_2[PdX_4]$ complexes without a base

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ABSTRACT

An efficient method was developed for the oxidative Heck reaction between arylboronic acids and olefins catalyzed by anionic palladium complexes of the type $[CA]_x[PdCl_4]$ ($x = 1,2$) and $[CA]_2[Pd_2Cl_6]$ (CA = imidazolium or pyridinium cation). Molecular oxygen was employed as an environmentally benign oxidant to regenerate Pd(II) species during the reaction. The elaborated protocol could be applied to the coupling of different arylboronic acids with both electron-rich and electron-poor olefins. The catalyst system was further employed for the one-pot oxidative Heck reaction followed by the Heck coupling to build conjugated compounds in good yield.

Mass spectrometry (ESI–MS) and UV–vis spectroscopy was used to identify palladium-containing complexes in the reactions. A plausible reaction mechanism of the oxidative Heck reaction was proposed.

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1. Introduction

Structural motifs of arylated olefins are present in natural products, pharmaceuticals, and other organic materials [1–8]. One of the standard tools used for the preparation of arylated olefins is the Heck reaction, which is the palladium-catalyzed coupling of an aryl halide and an olefin [1–8]. Despite its high potential and many applications, this reaction has some drawbacks such as harsh reaction conditions, the requirement of an inert atmosphere, and the generation of hydrogen halide as a byproduct [1–10]. In addition to the conventional Heck reaction, olefins can also be arylated by the use of nucleophilic organometallic reagents such as aryl derivatives of silicon [11–14], antimony [15], and tin [16–20]. Unfortunately, these organometallic reagents and their byproducts are highly toxic and difficult to separate from the final product. Therefore, another method, the oxidative Heck reaction, based on the coupling of arylboronic acid and an olefin (Fig. 1) has received increasing attention. The advantages of this procedure consist in the elimination of a halide from the reaction mixture and very often milder conditions than in the original Heck reaction.

The oxidative Heck reaction in a stoichiometric version was first described by Heck in 1975 [6]. Investigations of the reaction mechanism have shown that an oxidant is required for the efficient catalytic coupling of the olefin with arylboronic acid [21–37]. Accordingly, it has been proposed that palladium(II) is the catalytically active species, and the application of $Cu(OAc)_2$ as an oxidant regenerating the catalytic amount of Pd(II) from Pd(0) has been described [21–25]. Later, protocols for the oxidative Heck reaction with silver salts as oxidants have been developed [26–28]. Promising results have also been obtained in systems containing $Pd(OAc)_2$ and quinine [29,30] or DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) [31] as well as using $Ni(acac)_2$ and TEMPO [66].

In 2003, Jung discovered that O_2 could act as an efficient oxidant of palladium in the catalytic cycle [32], and in 2006 he published the base-free oxidative Heck-type reaction with improved selectivity [33]. Up to now, only a few palladium(II) systems have been used in the oxidative Heck reaction without a base [34–36,41]. On the other hand, in order to get satisfactory results in the oxidative Heck-type reaction with simple palladium precursors and O_2 as an oxidant, the employment of nitrogen [36–39] or phosphorous ligands [40,42] is necessary. The oxidative coupling of arenes with olefins has also been performed under O_2 [43] and promising results have been noted with air used instead of O_2 [31,39].

A relatively small number of premade palladium(II) complexes have been employed for the Heck-type reaction under an O_2 atmosphere [34,36,44]. For example, a palladium complex with N,N-dimethylethanolamine [36], a dimeric tridentate NHC-amidate-alkoxidepalladium(II) [34] and imidazole-based SPO (secondary phosphine oxide ligands) complexes [65] have been successfully applied in the asymmetric Heck-type reaction.

In this paper, we present the studies of the oxidative Heck-type reaction catalyzed by anionic palladium complexes of the

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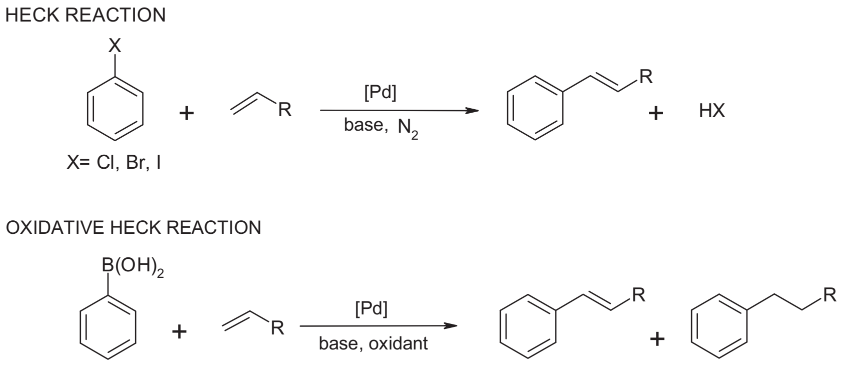


Fig. 1. Scheme of Heck and oxidative Heck reactions.

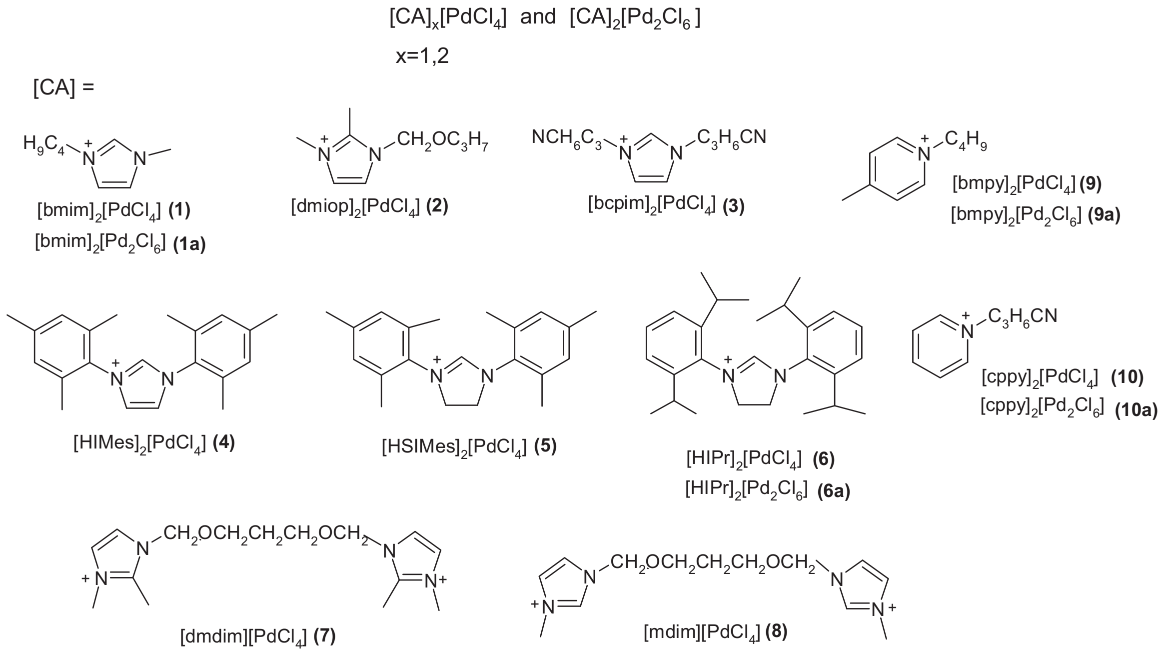


Fig. 2. Anionic palladium(II) complexes.

type $[CA]_x[PdCl_4]$ and $[CA]_2[Pd_2Cl_6]$ ($x = 1$ or 2) and $[CA]_2[Pd_2Cl_6]$ (IL = imidazolium or pyridinium cation) (Fig. 2).

Considering the very good catalytic activity of these complexes in methoxycarbonylation [45] and in the Suzuki reaction [46,47] in which $PhB(OH)_2$ was used as a substrate, we also expected good results in the oxidative Heck-type reaction.

Air-stable anionic Pd(II) complexes can be easily prepared using any imidazolium or pyridinium salt. In addition, the presence of $[CA]^+$ cations of different steric hindrance can influence the catalytic reaction course, as it had already been observed earlier [46,47]. On the other hand, the use of ionic liquids in a catalytic reaction can be controversial because of their potential toxicity [67,68].

We decided to test a group of anionic palladium complexes with the aim of elaborating an efficient and simple catalytic procedure that could be applied for a variety of substrates. To that aim, not only conventional heating but also microwave energy was used.

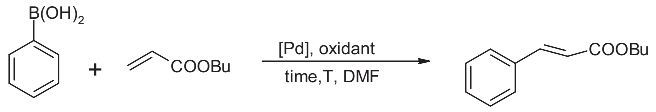


Fig. 3. Oxidative Heck-type reaction of phenylboronic acid and n-butyl acrylate.

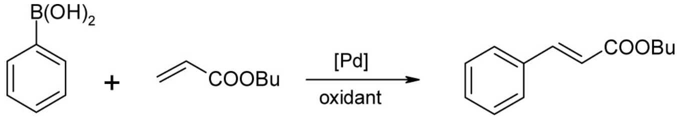
2. Results and discussion

2.1. Optimization of oxidative Heck reaction conditions

In the initial step of our studies, we tested different palladium precursors and oxidants in a model reaction of butyl acrylate with phenylboronic acid at 130 °C over 4 h (Fig. 3). In reactions performed under base-free conditions, one product, butyl cinnamate, was selectively formed. In contrast, in reactions catalyzed by **cat. 9** in the presence of K_2CO_3, selectivity was lower and a side product, butyl 3-phenylpropanoate, was found besides the major product (Table 1, entry 6, 7). A similar negative influence of the base on reaction selectivity has also been reported for other catalytic systems [26,64].

Three different oxidants were employed in test reactions, namely air, O_2 and $Cu(OAc)_2$. In almost all cases, independently of the kind of palladium precursor used, O_2 gave the best results providing the highest yield of the product. It should be underlined here that all the experiments were performed under low pressure, 1 atm only from a baloon. The highest yield, 83% was achieved after 4 h with **cat. 9** (Table 1, entry 5), and the prolongation of the reaction time to 24 h resulted in a yield increase to 98%. Two other palladium precursors containing a chloride ligand, $PdCl_2$ and

Table 1
Optimization of the oxidative Heck reaction with different palladium complexes and oxidants.



Entry	Oxidant catalyst	conversion [%][*]			Time [h]
		air	O_2	$Cu(OAc)_2$	
1	$PdCl_2$	18	60	30	4
2	$PdCl_2$(cod)	10	63	44	4
3	Pd_2dba_3	15	23	10	4
4	$Pd(OAc)_2$	21	33	65	4
5	**Cat.9**	21	83	50	4
6	**Cat.9**/K_2CO_3	14/16[a)]	22/30[a)]	21/38[a)]	4
7	**Cat.9**/K_2CO_3	20/29[a)]	78/80[a)]	32/43[a)]	24

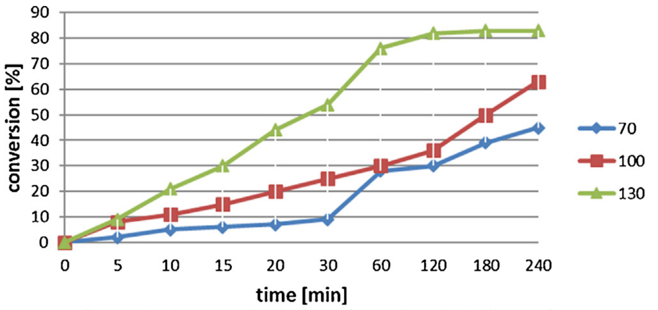
Reaction conditions: butyl acrylate (1 mmol), phenylboronic acid (1.5 mmol), [Pd] (2 mol%), DMF (5 mL), 130 °C, 4 h, $Cu(OAc)_2$ (2 mmol).
a) Conversion to butyl cinnamate/total conversion.
[*] Estimated by GC.

$PdCl_2$(cod) (Table 1, entry 1, 2) also formed good amounts of butyl cinnamate, 60% and 63%. Similarly as was noted earlier by other authors, $Pd(OAc)_2$ worked efficiently in the presence of $Cu(OAc)_2$ [11] (Table 1, entry 4); however, with other oxidants, the results were not satisfactory. Air appeared to be an insufficient oxidant, providing 21% of the product in the best case.

A relatively low yield obtained with $Pd_2(dba)_3$ as the catalyst precursor (Table 1, entry 3) indicated a preference for Pd(II) over Pd(0) in the reaction studied. In particular, $Pd_2(dba)_3$ was not very efficient, while it worked very well in the oxidative Heck reaction performed with the addition of a base [37]. According to the literature [48], $Pd_2(dba)_3$ can be considered a mixture of a Pd(0) complex and Pd(0) nanoparticles, and most probably those forms were not suitable for catalysis under the applied conditions Table 1.

2.2. *Effect of temperature and reaction time*

The optimization of the reaction conditions, first temperature, was performed for **cat. 9**. The temperature dependence, presented on Fig. 4, shows the absence of an induction period in the studied reaction, and consequently, ca. 10% of the product was formed after 5 min. It can, therefore, be supposed that the eventual transformation of the palladium precursor to a catalytically active form is relatively fast. As expected, a higher temperature facilitated the formation of the products and the highest yield, 83%, was obtained at 130 °C. At 70 °C, the yield was 45% after 4 h, and it increased only to 55% after 24 h.



Reaction conditions: butylacrylate(1mmol), phenylboronic acid (1.5 mmol), cat.9 (2 mol%), DMF (5 mL), O_2, 4 h.

Fig. 4. Kinetic profile of the oxidative Heck reaction in different temperatures.

Table 2
Oxidative Heck reaction in different solvents.

solvent	conversion [%][a]					
	2-propanol	2-propanol/ H_2O	H_2O	THF	DMSO	NMP
	4	1	22	5	26	60

Reaction conditions: butyl acrylate (1 mmol), phenylboronic acid (1.5 mmol), **cat.9** (2 mol%), solvent (5 mL), O_2 atmosphere, 130 °C, 4 h.
[a] Estimated by GC.

2.3. *Effect of the solvent*

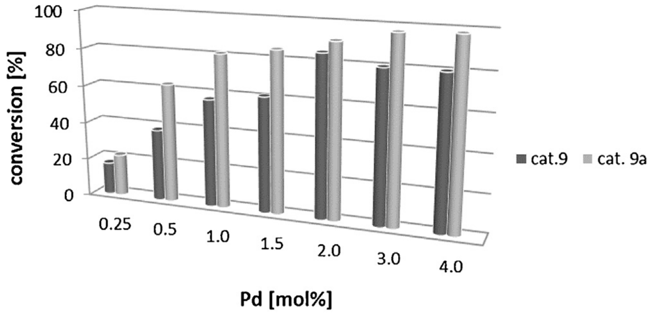
Not only temperature but also the kind of solvent influenced the yield of butyl cinnamate. The reaction studied can be efficiently performed in DMF, and a good yield, 60%, was also obtained in NMP (Table 2). Other tested solvents were not very suitable for the efficient formation of the product. Interestingly, 22% of butyl cinnamate was formed in water in which **cat. 9** was completely insoluble.

On the other hand, 2-propanol and a 2-propanol/water mixture made it possible to obtain only traces of the product, while these solvents worked very well in the Suzuki–Miyaura cross-coupling catalyzed by anionic palladium complexes [46,47].

2.4. *Effect of the catalyst amount*

Studies of the concentration effect resulted in finding the optimal amount of the catalyst, which was estimated to be 1–2% mol. An increase in the product yield with the increase in the catalyst amount (Fig. 5) warranted the conclusion that the reaction is catalyzed by a soluble Pd(II) species rather than by Pd(0) nanoparticles, which is the preferred catalyst for many cross-coupling reactions [1–10]. When Pd(0) nanoparticles are involved in the catalytic process, non-linear dependence of the product yield versus palladium amount is expected, with characteristic yield decrease at higher palladium concentrations [49]. This was explained by agglomeration of Pd(0) nanoparticles leading to decrease of their activity at higher concentration. Actually, it can be assumed that such non-linear yield dependence on the Pd amount indicated on the important role of Pd(0) nanoparticles in the reaction [49]. In the studied system, the participation of Pd(0) nanoparticles in the reaction course seems to be rather limited because even a high concentration of palladium did not result in reaction inhibition.

It should be noted here that the dimeric **cat. 9a** gave better results in all experiments than the monomeric cat.9 when the same palladium amount was used. One possible explanation could be splitting of the dimers under reaction conditions with formation coordinatively unsaturated species of higher activity. Alternatively, activation of substrates on two, situated closely palladium centers could accelerate the reaction course.



Reaction conditions: butylacrylate (1 mmol), phenylboronic acid (1.5 mmol), DMF (5 mL), O_2, 130°C, 4 h.

Fig. 5. Effect of palladium amount on oxidative Heck reaction course.

Table 3
The oxidative Heck reaction catalyzed by $[CA]_x[PdCl_4]$ or $[CA]_2[Pd_2Cl_6]$ complexes.

	conversion [%][a]		
$[CA]^+$	$[CA]_2[PdCl_4]$	$[CA]_2[Pd_2Cl_6]$	$PdCl_2(cod) + [CA]Cl$
bmim	74	98	38
dmiop	54		42
bcpim	72		30
HIMes	88		63
HSIMes	79		48
HIPr	78	86	24
dmdim	65		21
mdim	40		19
bmpy	83	91	36
cppy	72	80	40

Reaction conditions: butyl acrylate (1 mmol), phenylboronic acid (1.5 mmol), [Pd] (2 mol%), DMF (5mL), O_2 atmosphere, 130 °C, 4 h.

[a] Estimated by GC.

2.5. *Effect of the O_2 concentration*

After the selection of O_2 as the preferred oxidant, we optimized the procedure of its introduction to the reactor. When the catalytic reaction was performed with a balloon filled with O_2 and connected to the Schlenk tube, the results were often not fully reproducible. Most probably, it was caused by the transfer of some amount of the reactants to the balloon at the reaction temperature (130 °C). Further experiments showed that the yield of butyl cinnamate remarkably increased when O_2 was bubbled through the solvent (DMF) before the reaction. For an efficient catalytic process, it was enough to use the solvent saturated with O_2 and to perform the reaction in the Schlenk tube filled with O_2. The volume of O_2 in the Schlenk tube was sufficient for the catalytic reaction, and the balloon was not needed. It was also checked that 5 min of saturation of DMF with O_2 already guaranteed the formation of the product with 80% yield. The prolongation of the saturation time to 10 or 60 min in fact had no further influence on the reaction course.

On the other hand, when DMF not saturated with O_2 was used, the reaction yield was lower, and only 59% of the product was formed. When DMF was saturated with N_2 instead of O_2, the yield was only 9%.

The elaborated experimental procedure, involving the use of a solvent saturated with O_2 and Schlenk tube filled with O_2 is quite simple. Thus, the reaction can be performed without the balloon.

2.6. *Catalytic activity of different Pd(II) complexes*

An optimized procedure was next used for testing the catalytic activity of all the synthesized anionic complexes. Accordingly, reactions were performed at 130 °C, using 2 mol% [Pd] in DMF saturated with O_2. The results shown in Table 3 evidence the good or very good catalytic performance of monomeric as well as dimeric precursors. It should be underlined that the catalytic results are slightly influenced by the kind of cation present in the anionic complexes. In particular, complexes containing imidazolium or pyridinium cations performed good. It is interesting because only imidazolium complexes were active in the Suzuki–Miyaura cross-coupling while pyridinium cations showed a strong inhibiting effect [45]. The highest yield was noted for dimeric complexes $[bmim]_2[Pd_2Cl_6]$ (**cat. 1a**) (98%) and for $[bmpy]_2[Pd_2Cl_6]$ (**cat. 9a**) (91%). The best monomeric catalysts, **cat. 9** ($[bmpy]_2[PdCl_4]$) and **cat. 4** ($[HIMes]_2[PdCl_4]$), formed 83% and 88% of butyl cinnamate. Thus, the steric hindrance of the cation had positive influence on the product yield. Interestingly, a reaction catalyzed by $PdCl_2(cod)$ and ionic liquids ([CA]Cl) in all cases produced significantly worse results than premade anionic complexes. One possible explanation of that could be too slow formation of palladates under in situ conditions.

2.7. *Effect of substrates: olefins and arylboronic acids*

The oxidative Heck-type reactions were next performed using different olefins and three catalysts **cat. 9**, **cat. 9a**, and **cat. 1a** (Table 4). Methyl acrylate, styrene, and allylbenzene reacted very well producing the expected products with a high selectivity. In reactions with cyclic olefins as substrates, the selectivity was lower, and two products were formed for cyclohexene-3-on (Table 4, entry 2) and for cyclohexene (Table 4, entry 4). The saturated ketone, found in the reaction of cyclohexene-3-on, was formed via conjugate addition reaction involving intermediate form in which ketone coordinated to palladium via Pd-O bond [69]. The isomerization of the arylated cycloheptene resulted in the formation of four products in comparable amounts (Table 4, entry 6). Only a small increase in the product yield was achieved after the prolongation of the reaction time to 7 h. Under the applied conditions, cyclopentene did not react with phenylboronic acid.

In order to estimate the scope and the limitations of the elaborated procedure, a series of arylboronic acids were used for coupling with butyl acrylate (Table 5) in the presence of **cat. 9** and O_2 as an oxidant. For comparison, reactions with $Cu(OAc)_2$ instead of O_2 as an oxidant were also performed. Moreover, in one series of experiments, microwave induction was used instead of conventional heating.

In all cases, reactions with O_2 gave better results than those with $Cu(OAc)_2$, confirming the good applicability of our procedure. Reactions performed under microwave irradiation in an O_2 atmosphere also gave good results already after 3 h. It should be pointed out that the successful application of microwaves was possible because the amount of O_2 present in the Schlenk tube was suitable for the reaction.

High yields of the coupling products were obtained using boronic acid with an electrodonor group (Table 5, entries 3–7). The presence of a -Br substituent in position 2 or 4 of the phenyl ring did not influence the yield of the product when O_2 was used as an oxidant (Table 5, entries 8 and 9). On the other hand, a reaction with $Cu(OAc)_2$ 4-bromophenylboronic acid offered better performance than with 2-bromophenylboronic acid Table 5.

In order to get more information about the catalyst stability and the applicability of the system, a two-step reaction in one-pot was performed. First, using the oxidative Heck procedure, (E)-butyl 3-(2-bromophenyl) acrylate was obtained. Next, the base K_2CO_3 and a new portion of butyl acrylate were added to the reaction mixture. The second step, performed according to the Heck mechanism, resulted in the formation of a (2E,2′E)-3,3′-(1,2-phenylene) bis[2-propenoic acid] dibutyl ester with 80% yield (Scheme 1).

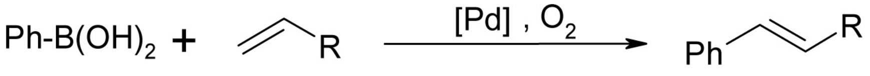
In an analogous experiment, (E)-butyl 3-(4-bromophenyl) acrylate reacted with 62% yield.

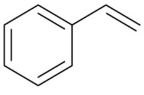
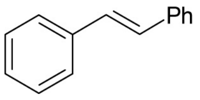
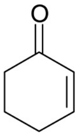
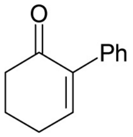
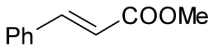
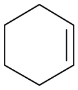
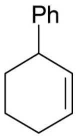
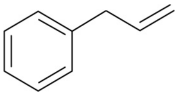
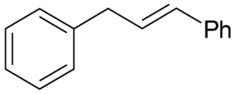
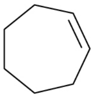
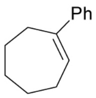
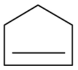
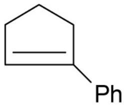
It can, therefore, be concluded that **cat. 9** after an oxidative Heck reaction is still active and, in particular, can be applied in the Heck cross-coupling with a very good result. The first coupling is very selective, without the formation of the Heck product. The final product was formed with good yield without the separation of an intermediate cinnamate.

2.8. *UV–vis monitoring of O_2 activation*

The performed studies clearly showed that O_2 played an important role in the catalytic cycle. We selected UV–vis spectroscopy as a tool to monitor the reaction of $[bmpy]_2[PdCl_4]$ with O_2 at 130 °C. The first spectrum showed a weak band at 336 nm characteristic of a $[PdCl_4]^{2-}$ anion (Fig. 6). When the solution was heated under an O_2 atmosphere, this band disappeared, and a new band was

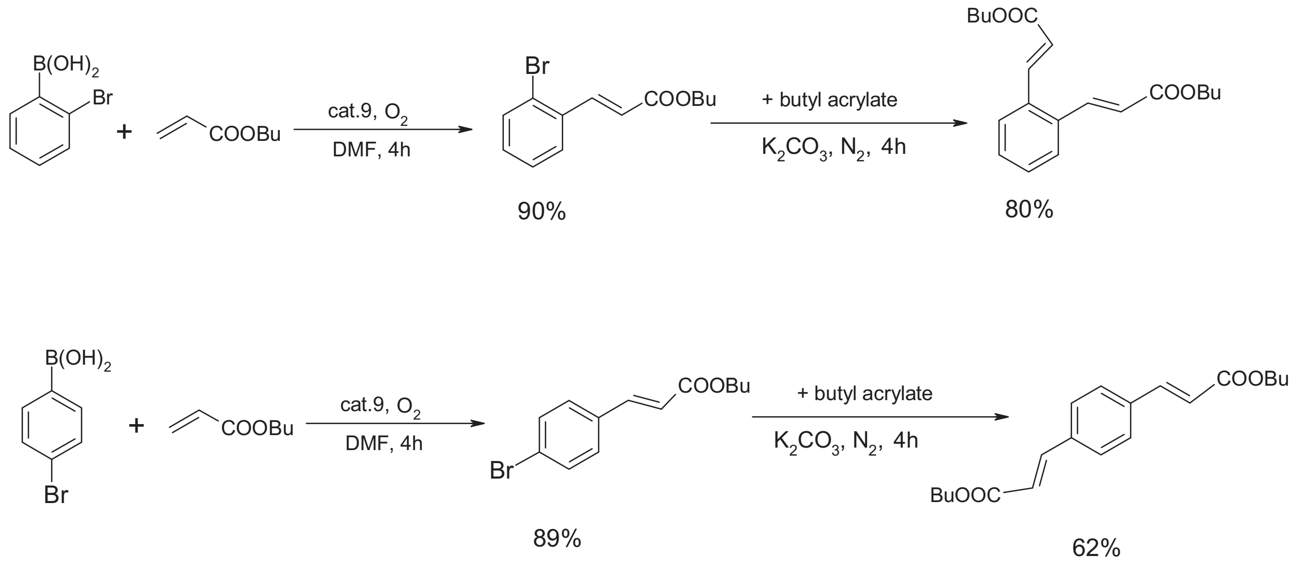
Table 4
The oxidative Heck reaction of phenylboronic acids with various olefins.



			conversion [%][a]			
			Cat.9		**Cat.9a**	**Cat.1a**
Entry	Olefin	Product	4 h	7 h	4 h	4 h
1			65	68	79	78
2			48	52	65	46
			27	20	34	18
3			88	93	98	98
4			36	38	19	26
			15	18	4	11
5			94	89	85	60
6			12	9	12	12
			13 23 19	10 17 114	13 24 19	13 23 19
7			0	0	0	0

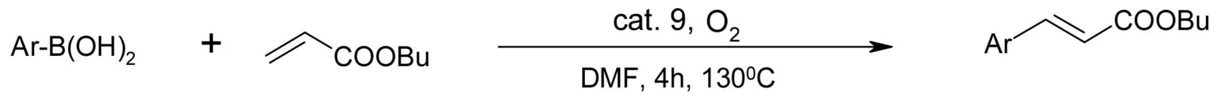
Reaction conditions: olefin (1 mmol), phenylboronic acid (1.5 mmol), [Pd] (2 mol%), DMF (5 mL), O_2 atmosphere, 130 °C,4 h.

[a] Estimated by GC.



Scheme 1. One-pot oxidative Heck reaction and Heck reaction.

Table 5
The oxidative Heck reaction of butyl acrylate with arylboronic acids.



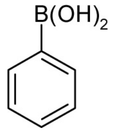
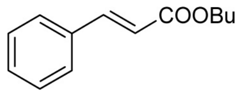
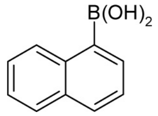
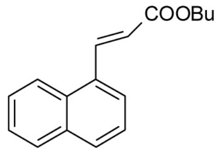
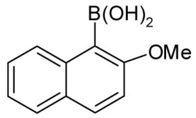
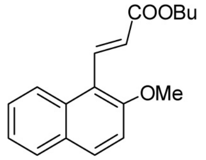
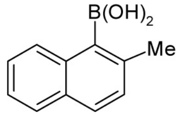
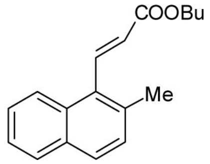
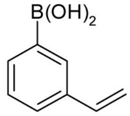
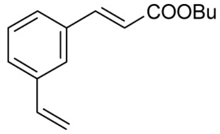
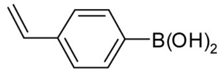
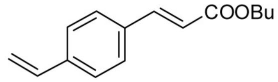
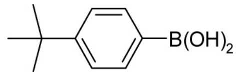
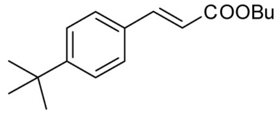
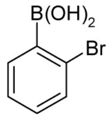
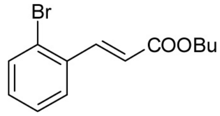
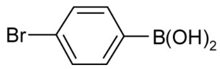
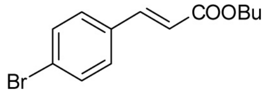
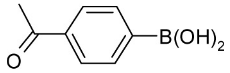
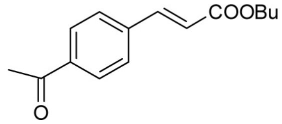
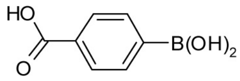
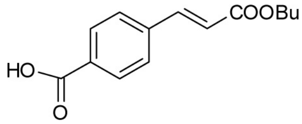
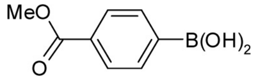
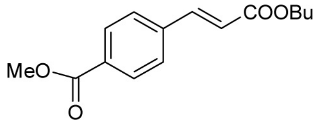
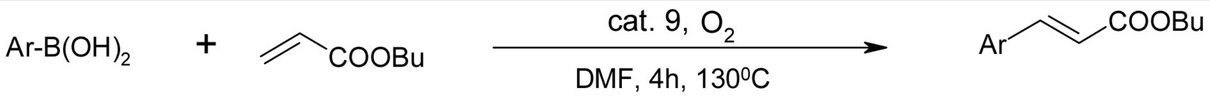
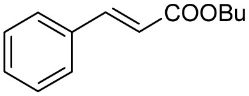
Entry	Ar-B(OH)$_2$	Product	O$_2$	Cu(OAc)$_2$	MW[a)]
1			83	50	85
2			80	50	81
3			49	16	47
4			80	0	79
5			49	23	50
6			50	36	51
7			80	51	80
8			90	31	96
9			89	51	89
10			82	15	83
11			0	0	0
12			37	25	43

Table 5 (*Continued*)



Entry	Ar-B(OH)$_2$	Product	O$_2$	Cu(OAc)$_2$	MW$^{a)}$
13	$Na[BPh_4]$		80	46	80

Reaction conditions: butyl acrylate (1 mmol), arylboronic acid (1.5 mmol), **cat.9** (2 mol%), DMF (5 mL), O_2 atmosphere, 130 °C, 4 h.
a) 3 h reaction.

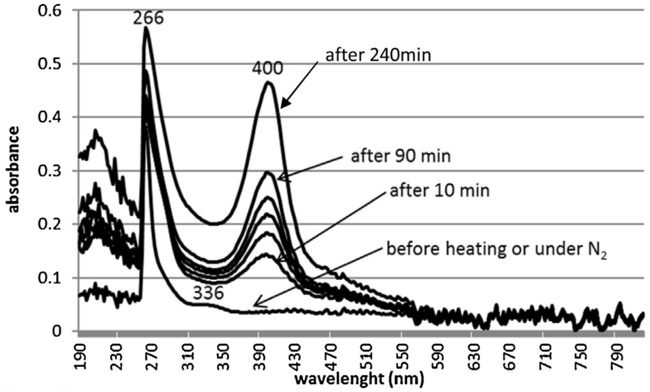


Fig. 6. UV–vis absorption spectra monitoring the reaction of **cat. 9** with O_2 at 130 °C in DMF.

formed at 400 nm, with the intensity increasing over time. Similar changes were also observed for the sample heated in air, although the absorption increase was slower.

In the spectrum of the solution of **cat. 9a** saturated with O_2, a new band appeared at 408 nm confirming the formation of a new species.

In contrast, practically no changes in the UV–vis spectrum were noted when a solution of **cat. 9** in DMF was heated under N_2. The formation of a new band was also inhibited in the presence of substrates, and, for example, no effect was observed when butyl acrylate was present in the solution. It can be anticipated that O_2 will compete with olefin for place in the coordination sphere of palladium.

As far as we know, the activation of O_2 on palladate complexes has not been described before. On the other hand, it has been shown by experimental and theoretical methods that Pd(0) complexes with phosphines or chelating nitrogen ligands react with O_2 preferably forming η^2-peroxo Pd(II) complexes [50–56]. In the reaction of a Pd(I) dimer with O_2, the formation of a bridging peroxo ligand has been proposed [57]. Scarce examples of reactions of Pd(II) complexes with O_2 leading to Pd(IV) complexes have been published [58,59]. In our system, however, the observed changes in UV–vis spectrum do not indicate the presence of Pd(IV).

2.9. *ESI–MS measurements*

ESI–MS spectra were measured in DMF solutions heated to 130 °C in an O_2 atmosphere (Table 6). In all cases, the signals originating from palladium-containing fragments were observed in the MS(−) part of the spectrum while only the $[bmpy]^+$ cation was observed in the MS(+) region. The spectrum of **cat. 9** showed signals typical for anionic complexes, composed of palladium and Cl^- ligands.

Table 6
ESI–MS(−) data of palladium species obtained in the reaction of **cat.9** + O_2 and **cat.9** + substrates + O_2 in DMF.

Cat.9 [m/z]		**Cat.9** + PhB(OH)$_2$ + butyl acrylate [m/z]	
$[PdCl_3]^-$	212.8	$[HPdCl(butyl\ acrylate)(Ph)]^-$	347.0
$[PdCl_2]$	177.8	$[HPdCl_2(butyl\ acrylate)]^-$	306.9
$[PdCl]^-$	141.9	$[PdCl_3]^-$	212.8
		$[PdCl_2]$	177.8
		$[PdCl]^-$	141.9

Reaction conditions: butyl acrylate (1 mmol), phenylboronic acid (1.5 mmol), cat.9 (2 mol%), DMF (5 mL), O_2 atmosphere, 130 °C, 4 h.

The analysis of the second solution, containing **cat. 9**, PhB(OH)$_2$ and butyl acrylate, made it possible to identify fragments in which substrates were coordinated to palladium. Interestingly, the simultaneous coordination of butyl acrylate and the phenyl group to the same palladium ion was confirmed. In all palladium species, a Cl^- anion was also present indicating its important role in the catalytic cycle.

2.10. *Mercury test*

The mercury test is often used in order to distinguish between the reaction pathway with Pd(0) nanoparticles and a truly homogeneous reaction catalyzed by soluble complexes [60,61]. Using this test, we aimed to prove the dominating role of Pd(II) anionic species in the catalytic process. In this case, the reaction should be not affected by Hg(0). Fig. 7 presented results obtained in four different experiments in which Hg(0) was added to the reaction mixture after 5, 10, 20 or 30 min. Surprisingly, the oxidative Heck-type reaction was strongly inhibited by a 500-fold excess of Hg(0) as illustrated in Fig. 7.

The observed inhibiting effect could not be explained by the formation of an amalgam with Pd(0) nanoparticles catalyzing the reaction, because, according to the TEM analysis of the

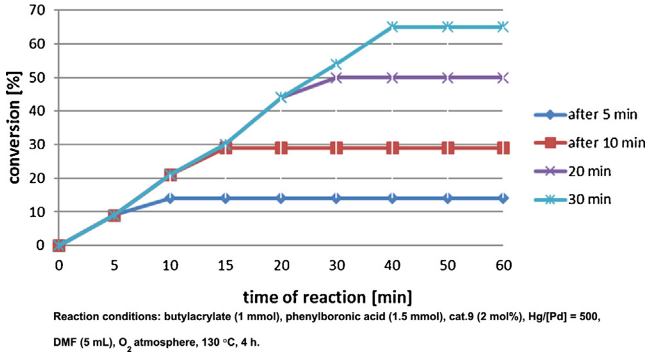


Fig. 7. Mercury test in the oxidative Heck reaction.

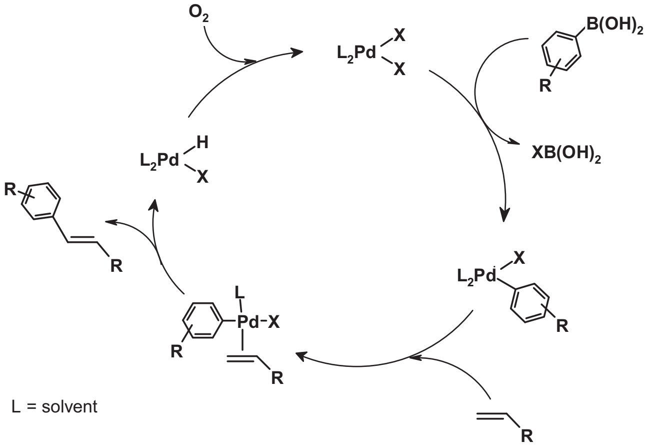


Fig. 9. Plausible mechanism of the oxidative Heck-type reaction.

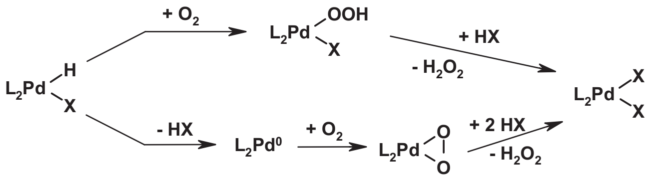


Fig. 8. Possible reactions of the Pd-H intermediate with O_2.

post-reaction mixture, Pd(0) nanoparticles were not present in a measurable amount.

An alternative explanation of the observed mercury action could be the redox reaction of Pd(II) with Hg(0) resulting in the formation of Pd(0) and, in consequence, in the elimination of the catalytically active palladium form. A similar reaction was described for Pt(II) [62]. In order to prove such a hypothesis, the stoichiometric reaction of **cat.9** and Hg(0) was performed. As expected, after 30 min. of warming, the solution became colorless and the Hg metal disappeared. Thus, the reduction of Pd(II) by Hg(0) is responsible for the retardation of the catalytic reaction.

2.11. *Reaction scheme*

A plausible mechanism for the oxidative Heck-type reaction in the studied system, inspired by literature examples [31,36,44], is shown in Fig. 9.

The most critical step in this mechanism is the elimination of the hydrido-palladium intermediate, $[HPdCl_3]^-$, to recover a Pd(II) species suitable for the next catalytic cycle. Two feasible pathways of the Pd-H transformation can be proposed [51,63]. The first one consists in the reductive elimination of HCl followed by the Pd(0) oxidation with O_2, while the second one involves the insertion of O_2 into a Pd-H bond, leading to a Pd-OOH or Pd-OH fragment (Fig. 8).

We did not observe the formation of black palladium during the catalytic reaction and, in addition, Pd(0) was not active under our reaction conditions. Therefore, it can be proposed that recovering the catalyst consists in the reaction of a Pd-hydrido species with O_2, enabling the formation of L_2PdCl_2 suitable for the next catalytic cycle.

3. Conclusions

An efficient catalyst system was developed for the oxidative Heck-type reaction between arylboronic acids and various olefins under base- and ligand-free conditions. Monomeric and dimeric anionic palladium complexes of the type $[CA]_x[PdCl_4]$ ($x = 1,2$) and $[CA]_2[Pd_2Cl_6]$, easily prepared and stable in the presence of oxygen and moisture, were used as catalysts for this reaction. The application of oxygen (1 atm), instead of copper or silver salts, as a reoxidant of palladium simplified the procedure.

According to the designed procedure, electron-donating and electron-withdrawing arylboronic acids and olefins reacted over 4 h or 3 h with the use of microwaves, giving the desired product in high yields.

A one-pot reaction composed of oxidative Heck and normal Heck reactions was successfully applied for the synthesis of double substituted arenes. It was also confirmed that after the first step, the palladium catalyst was still active and could be used under the Heck conditions.

Using ESI–MS and UV–vis methods, some palladium(II) intermediates were identified. In particular, the ability of anionic complexes to activate O_2 was confirmed for the first time.

4. Experimental

All reactants were obtained from Aldrich, Fluka or Merck in "for synthesis" quality or higher, and were used as received without further purification or drying.

Ionic liquids: [dmiop]Cl, $[dmdim]Cl_2$ and $[mdim]Cl_2$ were obtained from prof. J. Pernak, Technical University Poznań.

Palladium complexes $[bmim]_2[PdCl_4]$, $[mioe]_2[PdCl_4]$, $[dmiop]_2[PdCl_4]$, $[bcpim]_2[PdCl_4]$, $[HIPr]_2[PdCl_4]$, $[HSIMes]_2[PdCl_4]$, $[HIMes]_2[PdCl_4]$, $[dmdim][PdCl_4]$, $[mdim][PdCl_4]$, $[bmpy]_2[PdCl_4]$ were obtained according to methods described in the literature [45–47].

4.1. *Synthesis of palladium complexes*

4.1.1. *$[cppy]_2[PdCl_4]$ (cppy = 1-(3-cyanopropyl) pyridinium cation)*

0.36 g (2.0 mmol) of [cppy]Cl was added to the solution of 0.28 g (1.0 mmol) $PdCl_2$(cod) in hot CH_3CN (5 mL). The mixture was heated for 15 min, until the yellow solution became red. The solution was cooled to room temperature and solvent was removed under reduced pressure. The product was precipitated by addition of diethyl ether (2–3 mL). Product yield: 85%; anal. calcd. for $PdCl_4C_{18}H_{22}N_4$: C 39.8, H 4.1, N 10.3%; found: C 39.1, H 3.7, N 10.0%; ^1H NMR (CD_3CN): $\delta = 8.98$ (t, $J = 7.8$, 2H, CH_2), 8.59 (d, $J = 7.8$, 4H, Ar-H), 7.36 (t, $J = 7.8$, 4H, Ar-H), 4.04 (m, $J = 7.8$, 4H, CH_2), 2.14 (m, $J = 7.8$, 4H, CH_2), 1.87 (t, $J = 7.8$, 4H, CH_2); ^{13}C NMR (CD_3CN): $\delta = 148$ (C_{Ar}-H), 146 (C_{Ar}-H), 130 (C_{Ar}-CH_3), 119 (-CN), 53 (CH_2), 25 (CH_2), 15 (CH_2).

4.1.2. *$[cppy]_2[Pd_2Cl_6]$*

0.18 g (1.0 mmol) of [cppy]Cl was added to the solution of 0.28 g (1.0 mmol) $PdCl_2$(cod) in hot CH_3CN (5 mL). The mixture was heated for 30 min, until the yellow solution became red. The solution was cooled to room temperature and solvent was removed under reduced pressure. The product was precipitated by addition of diethyl ether (2 mL). Product yield: 66%; anal. calcd. for $Pd_2Cl_6C_{18}H_{22}N_4$: C 30.0, H 3.1, N 7.8%; found: C 29.6, H 3.0, N 7.8%; ^1H NMR (CD_3CN): 8.97 (t, J=7.05, 4H, Ar-H), 8.65 (d, J = 7.0, 4H,Ar-H), 7.40 (t, J = 7.05, 2H, Ar-H), 4.11 (t, J = 6.9, 4H, CH_2), 2.16 (m, J = 6.9, 4H, CH_2), 1.87 (t, J = 6.8, 4H, CH_2); ^{13}C NMR (CD_3CN): $\delta = 149$ (C_{Ar}-H), 145 (C_{Ar}-H), 132 (C_{Ar}-CH_3), 119 (-CN), 51 (CH_2), 23 (CH_2), 15 (CH_2).

4.1.3. *$[bmpy]_2[Pd_2Cl_6]$*

The complex was obtained according to the procedure given for $[cppy]_2[Pd_2Cl_6]$ using 0.28 g (1.0 mmol) of $PdCl_2$(cod) and 0.18 g (1.0 mmol) of [bmpy]Cl; yield: 95%; anal. calcd. for $C_{20}H_{32}N_2Pd_2Cl_6$: C 33.1, H 4.4, N 3.9%; found: C 32.8, H 3.7, N 3.8%; ^1H NMR (CD_3CN): $\delta = 8.71$, 8.45 (d, $J = 7.49$, 8H, Ar-H), 4.57

(t, J = 7.50, 4H, CH_2), 2.50 (m, J = 7.25, 4H, CH_2), 2.27 (m, J = 7.25, 4H, CH_2), 2.0 (s, 6H, CH_3), 1.12 (t, J = 7.30, 6H, CH_3); ^{13}C NMR (CD_3CN):δ = 161(CH3-C=) 145 (C_{Ar}); 129 (C_{Ar}); 61 (N-CH_2); 33 (Ar-CH_3); 21, 19(-CH_2-), 14(-CH_3).

4.1.4. *$[bmim]_2[Pd_2Cl_6]$*

The complex was obtained according to the procedure given for $[cppy]_2[Pd_2Cl_6]$ using 0.28 g (1.0 mmol) of $PdCl_2(cod)$ and 0.18 g (1.0 mmol) of [bmim]Cl; yield: 95%; anal. calcd. for $C_{16}H_{30}N_4Pd_2Cl_6$: C 27.3, H 4.3, N 7.9%; found: C 27.1, H 3.9, N 7.7%; ^1H NMR(CD_3CN) = 8.9 (s, 2H, N—CH=N); 7.6 (s, 2H, CH=CH); 7.5 (s, 2H, CH=CH); 4.2(t, J = 7.3, 4H, -N-CH_2); 3.9 (s, 6H, N—CH_3); 1.8(m, J = 7.5, 4H, -CH_2-); 1.4 (m, 4H, J = 7.5,

-CH_2-); 1.0(t, 6H, J = 7.5, -CH_3); ^{13}C NMR(CD3CN); =138 (N—CH=N); 126 (—CH=CH—); 122(CH=CH); 51 (N—-CH_3); 34 (—N—CH_2—); 31,29 (-CH_2-); 13(-CH_3).

4.1.5. *$[HIPr]_2[Pd_2Cl_6]$ (HIPr= 1,3-bis(2,6-diisopropylphenyl) imidazolinium cation)*

The complex was obtained according to the procedure given for $[cppy]_2[Pd_2Cl_6]$ using 0.28 g (1.0 mmol) of $PdCl_2(cod)$ and 0.39 g (1.0 mmol) of [HIPr]Cl; yield: 95%; anal. calcd. for $C_{54}H_{78}N_4Pd_2Cl_6$: C 53.8H 6.2, N 4.7%; found: C 53.0, H 3.3, N 4.3%;^1H NMR ($CDCl_3$): 8.36 (s, 2H, CH), 7.78 (s, 8H, CH_2-CH_2), 7.50 (t, J = 7.0, 4H,Ar-H), 7.12 (d, J = 6.9, 8H,

Ar-H), 2.87 (m, J = 6.9, 8H, CH), 1.20 (d, J = 6.9, 48H, CH_3), ^{13}C NMR(CD_3CN): δ = 140(N—CH=N); 137(C_{Ar}-H); 132(C_{Ar}-CH_3); 127(C_{Ar}-CH); 124(CH_2-CH_2); 117(-CH-); 27(CH_3); 22 (CH_3).

4.2. *Measurements*

^1H and ^{13}C NMR spectra were measured in CD_3CN on Bruker 500 spectrometers. UV–vis spectra were measured using Hewlett Packard 8452A Diode Array Spectrophotometer. Electrospray ionization mass (ESI–MS) spectra for synthesized compounds were recorded on a Bruker apex ultra FT-ICR. The products of the catalytic experiments were analyzed with a GC–MS (Hewlett Packard 8452A instrument). Experiments with microwaves heating were prepared in microwave oven (Anton Paar, Monowave 300, monomode, 850W max). Power of reactor is automatically adjusted depending on the reaction temperature.

4.3. *Typical procedure for the oxidative Heck reaction*

The oxidative Heck reaction was carried out in a 50 mL Schlenk tube. The solid substrates: phenylboronic acid (1.5 mmol, 0.184 g) and palladium complex (0.02 mmol) were weighted and placed in the Schlenk tube which was evacuated and filled with oxygen. Next, olefin (1 mmol) and 5 mL of the solvent saturated with oxygen (30 min) were added with a pipette in the atmosphere of oxygen. The reactor was closed with a rubber plug and the reaction mixture was stirred in 130 °C. After the given reaction time, the reactor was cooled down and the organic products were extracted with 20 mL of diethyl ether. For better phase separation 1 mL of water was added; 0.15 mL of mesitylene was added as an internal standard. The organic products were analyzed using the GC–MS method.

4.4. *Hg(0) test*

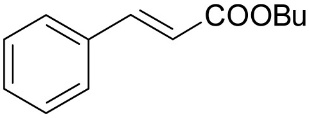
The oxidative Heck reaction was carried out as described above. After the specified reaction time, mercury (Hg/Pd = 500) was added and reaction was continued. Experimental data points have been obtained by sampling each of the four experiments at different times.

4.5. *One-pot reaction of oxidative Heck and Heck reaction*

The solid substrates: phenylboronic acid (1.5 mmol, 0.184 g) and palladium complex (0.02 mmol) were weighted and placed in the 50 mL Schlenk tube in the atmosphere of oxygen. Next, olefin (1 mmol) and 5 ml of the solvent saturated with oxygen were added with a pipette. The reactor was closed with a rubber plug and the reaction mixture was stirred in 130 °C. After 4 h the reaction was stopped and 2 mmol of K_2CO_3 and 1.0 mmol of butyl acrylate were added. In a nitrogen atmosphere the reaction mixture was stirred at 130 °C by next 4 h. After that time, the reactor was cooled down and the organic products were extracted with 20 mL of diethyl ether. For better phase separation 1 ml of water was added; 0.15 mL of mesitylene was added as an internal standard. The organic products were analyzed using the GC–MS method.

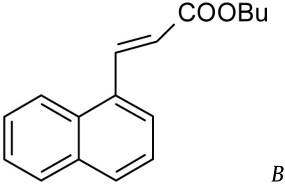
4.6. *Physical data for the following products:*

All compounds are determined by MS analysis and obtained results were compared with these published in the references [70–82].



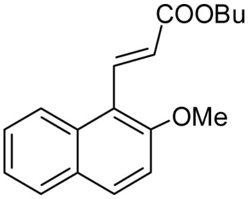
(E)-Butyl cinnamate

MS: m/z(%) = 41 (14), 51 (21), 103 (53), 131 (100), 148 (71), 204 ([M$^+$] 14) 70 – 75)



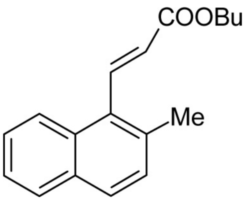
Butyl (E)-3-(naphthalen-1-yl) acrylate

MS: m/z(%) = 41 (22), 76 (22), 153(100), 181 (41), 198 (13), 254 ([M$^+$] 48) 72)



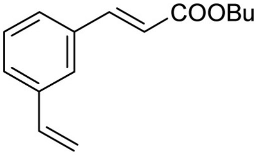
Butyl (E)-3-(2-methoxynaphthalen-1-yl) acrylate

MS: m/z(%) = 41(16), 82 (13), 167 (100), 195 (28), 268 ([M$^+$] 42) 72)



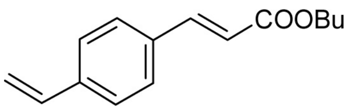
Butyl (E)-3-(2-methylnaphthalen-1-yl) acrylate

MS: m/z(%) = 152 (27), 167 (100), 195 (20), 268(23) 72)



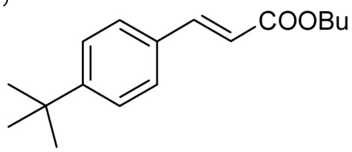
(E)- Butyl 3-(3-vinylphenyl) acrylate

MS: m/z(%) = 128 (51), 157(55), 174 (100), 230 ([M$^+$] 33) 71)



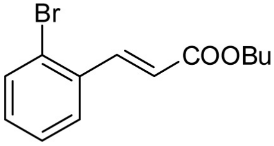
(E)- Butyl 3-(4-vinylphenyl) acrylate

MS: *m/z*(%) = 77 (14), 128 (54), 157 (58), 174 (100), 230, ($[M^+]$ 34) 71)



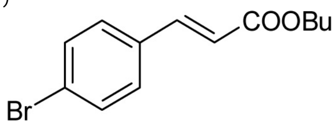
(E)- Butyl 3-(4-tert-butylphenyl) acrylate

MS: *m/z*(%) = 189 (39), 204 (16), 245 (100), 261 ($[M^+]$ 33) 73)



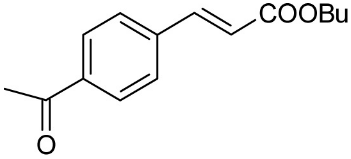
(E)-Butyl 3-(2-bromophenyl) acrylate

MS: *m/z*(%) = MS: m/z(%)=102 (79), 209 (45), 226 (100), 282([M+] 26) 75)



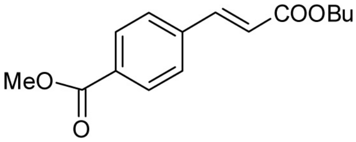
(E)-Butyl 3-(4-bromophenyl) acrylate

MS: *m/z*(%) = 102 (100), 209 (54), 226 (84), 282([M+] 21) 74,75)



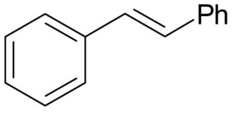
Butyl (E)-3-(4-acetylphenyl) acrylate

MS: *m/z*(%) = 42 (85), 102 (24), 131 (33), 175 (100), 191 (39), 231 (92), 246 ($[M^+]$ 18) 72,74,75)



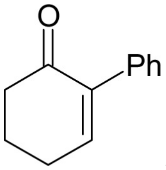
(E)-Methyl 4-(3-butoxy-3-oxoprop-1-en-1-yl) benzoate

MS: *m/z*(%) = 175 (83), 206 (100), 262 ($[M^+]$ 21) 72,75)



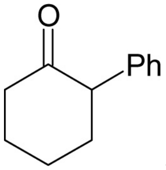
(E)-Stilbene

MS: *m/z*(%) = 76 (20), 89 (24), 165 (46), 180 ($[M^+]$ 100) 74,75)



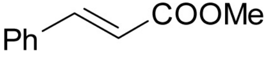
2-Phenyl-2-cyclohexen-1-one

MS: *m/z*(%) = 115 (75), 144 (100), 172 ($[M^+]$ 68) 77)



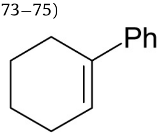
2-Phenylcyclohexanone

MS: *m/z*(%) = 104 (62), 117 (79), 131 (100), 174 ($[M^+]$ 74) 81,82)



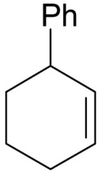
(E)- Methyl cinnamate

MS: *m/z*(%) = 51 (32), 77 (45), 103 (69), 131 (100), 162 ($[M^+]$ 59) 71,73–75)



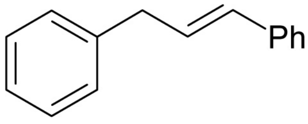
1-Phenyl-1-cyclohexene

MS: *m/z*(%) = 77 (23), 91 (35), 115 (52), 129 (100), 143 (52), 158 ($[M^+]$ 100) 76)



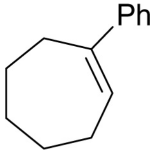
3-Phenyl-1-cyclohexene

MS: *m/z*(%) = 104 (100), 158 ($[M^+]$ 22) 78)



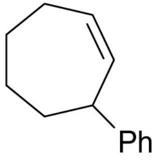
(E)-1,3-Diphenyl-2-propene

MS: *m/z*(%) = 115 (62), 179 (44), 194 ($[M^+]$ 100) 78)



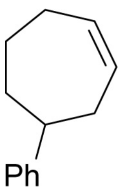
1-Phenylcycloheptene

MS: *m/z*(%) = 81 (46), 91 (65), 104 (100), 115 (46), 129 (85), 172 ($[M^+]$ 63) 79)



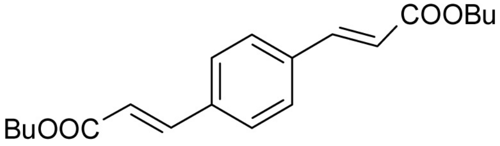
3-Phenylcycloheptene

MS: *m/z*(%) = 91 (54), 104 (100), 117 (82), 144 (36), 172 ($[M^+]$ 32) 79)



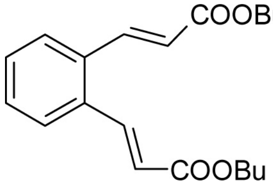
4-Phenylcycloheptene

MS: *m/z*(%) = 91 (68), 104 (82), 118 (71), 129 (100), 144 (57), 172 ($[M^+]$ 75) 79)



1,4-di(2-n-butoxycarbonyl-(E)-vinyl) benzene

MS: *m/z*(%) = 41 (23), 127 (26), 218 (100), 257 (43), 330 ($[M^+]$ 24) 80)



1,2-di(2-n-butoxycarbonyl-(E)-vinyl) benzene

MS: *m/z*(%) = 41 (76), 127 (76), 172 (100), 229 (27), 330 ($[M^+]$ 3) 80)

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