## Oxime Palladacycle-Catalyzed Suzuki–Miyaura Alkenylation of Aryl, Heteroaryl, Benzyl, and Allyl Chlorides under Microwave Irradiation Conditions

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Dedicated to the memory of Professor Rafael Suau.

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Abstract: A simple new protocol for the palladiumcatalyzed Suzuki-Miyaura cross-coupling of organic chlorides under microwave irradiation is presented. Deactivated aryl and heteroaryl chlorides are efficiently cross-coupled with alkenvlboronic acids and potassium alkenyltrifluoroborates using the 4,4'-dichlorobenzophenone oxime-derived palladacycle 1b as precatalyst in 0.1 to 0.5 mol% palladium loading, tris(tert-butyl)phosphonium tetrafluoroborate {[HP- $(t-Bu)_3$ ]BF<sub>4</sub>} as ligand, tetra-*n*-butylammonium hydroxide as cocatalyst, and potassium carbonate as base in N,N-dimethylformamide at 130°C under microwave irradiation conditions. Under these conditions, styrenes, stilbenes, and alkenylarenes are obtained in good to high yields, and with high regioand diastereoselectivities in only 20 min. The reported protocol is also very efficient for the regioselective alkenylation of benzyl and allyl chlorides to afford allylarenes and 1,4-dienes.

**Keywords:** alkenes; cross-coupling; homogeneous catalysis; microwave chemistry; palladacycles; Suzuki–Miyaura reaction

The Suzuki–Miyaura cross-coupling reaction constitutes one of the most powerful carbon-carbon bondforming transformations.<sup>[1]</sup> In recent years various modifications to this reaction have been made involving the nature of catalysts, solvents, bases, reaction conditions, and synthetic techniques. Particularly interesting aspected have resulted from advances in new catalyst development<sup>[2]</sup> which have enabled an expansion of the substrate scope of this reaction under low catalyst loading conditions to deactivated electrophiles such as aryl chlorides. Despite the overwhelming impact of the Pd-catalyzed Suzuki synthesis of biaryls in organic synthesis, the seemingly straightforward alkenylation of an aryl moiety has been, by comparison, overlooked.<sup>[3]</sup> Furthermore, from the two possible pair-wise combinations of aryl and alkenyl units, the cross-coupling between an aryl halide (or pseudohalide) and an alkenylboron nucleophile has been much less studied,<sup>[4]</sup> particularly in the case of the coupling of deactivated aryl chlorides.<sup>[5]</sup> Indeed, the Suzuki alkenylation of these interesting substrates has been scarcely considered, typically using high catalyst loadings (1–3 mol% Pd) and *trans*-styrylboronic acid as nucleophile.

Palladacycles<sup>[6]</sup> have been shown to be very efficient precatalysts for the Suzuki cross-coupling reaction.<sup>[7]</sup> In particular, we have recently demonstrated the high catalytic activity of oxime palladacycles **1**<sup>[8]</sup> (Figure 1) in the Suzuki–Miyaura synthesis of biaryls in organic<sup>[9]</sup> and aqueous solvents<sup>[10]</sup> using conventional heating or under microwave irradiation conditions. With respect to the alkenylation of aryl halides, a regio- and stereoselective synthesis of styrenes, stilbenes, and alkenylbenzenes<sup>[11]</sup> has been carried out in





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our group by coupling potassium vinyl- and alkenyltrifluoroborates with aryl bromides<sup>[12]</sup> and aryl chlorides<sup>[13]</sup> using oxime catalyst **1a** in refluxing water and DMF, respectively. Herein, we present a general protocol for the Suzuki–Miyaura alkenylation of deactivated aryl and heteroaryl chlorides with different boron compounds using palladacycle **1b** as catalyst under microwave irradiation conditions.

The activity of palladacycle 1b was initially studied in the Suzuki-Miyaura alkenylation of deactivated aryl chlorides using 4-chloroanisole and trans-styrylboronic acid as model substrates (Table 1). With this aim, the cross-coupling was performed using the reaction conditions previously optimized for the arylation of these demanding electrophiles in our group,<sup>[9b]</sup> that is, palladacycle 1b as catalyst in the presence of tris[tert-butyl]phosphonium tetrafluoroborate - [HP(t- $Bu_{3}BF_{4}^{[14]}$  – as ligand, tetra-*n*-butylammonium hydroxide (TBAOH) as additive, K<sub>2</sub>CO<sub>3</sub> as base, in DMF as solvent under microwave irradiation (40 W, 130°C) for 20 min. Under these conditions, the Suzuki product 2a was obtained in a 71% isolated yield. However, a moderate regioselectivity was observed in the cross-coupling process and, in a 14% yield, ipso-compound 3a was also obtained (Table 1, entry 1).<sup>[15]</sup> Compound **3a** is generated through a Heck-type addition-elimination mechanism where a  $\beta$ -hydrogen transfers to the terminal carbon. On the other hand, almost perfect regioselectivities in favour of the *cine* derivative **2a** were obtained with other different bulky and electron-rich phosphonium tetrafluoroborates (Table 1, entries 2–5), although the isolated yields were in all cases significantly lower than those obtained with  $[HP(t-Bu)_3]BF_4$  as ligand.

Next, the catalytic activity of palladacycle **1b** was compared with that of the 4-hydroxyacetophenone oxime-derived palladacycle **1a** (Figure 1) and other traditional Pd sources such as  $Pd(OAc)_2$ ,  $PdCl_2$ , and  $Pd_2(dba)_3$  under the optimized loading conditions. As depicted in Table 1, entries 6–9, all these catalysts presented lower activity in the cross-coupling reaction giving inferior yields than catalyst **1b**.

Finally, we examined the effect on the yield and the selectivity of the boron source. Thus, we carried out the coupling between 4-chloranisole and *trans*-2-phe-nylvinylboronic acid pinacol ester, potassium *trans*-2-phenylvinyltrifluoroborate,<sup>[16]</sup> and *trans*-2-phenylvinylboronic acid MIDA ester<sup>[17]</sup> under similar reaction conditions. As depicted in Table 1, entries 10–12, the reaction only worked with the pinacol ester and the potassium trifluoroborate still affording lower yields than the corresponding boronic acid although with better selectivities in favour of the *cine* compound **2a**.

To test the effectiveness of the catalytic system in the Pd-catalyzed alkenylation reaction, a range of deactivated aryl chlorides was examined using different alkenylboronic acids under the optimized reaction conditions (Table 2). A very similar yield and regiose-

 $\begin{array}{c} \mathsf{CI} \\ \mathsf{Ph} \\ \mathsf{OMe} \end{array} + \begin{array}{c} \mathsf{Ph} \\ \mathsf{Ph} \end{array} \overset{\mathsf{BX}}{\underset{\mathsf{OMe}}{\overset{\mathsf{I}}{\underset{\mathsf{Ph}}}} \mathsf{BX}} \overset{\mathsf{Pd} \text{ catalyst } (0.1 \text{ mol}\% \text{ Pd}), \\ (\mathsf{I}\mathsf{P}(\mathsf{R}^{1}\mathsf{R}^{2}_{2})]\mathsf{BF}_{4} \ (0.2 \text{ mol}\%), \\ \mathsf{TBAOH} \ (20 \text{ mol}\%), \mathsf{K}_{2}\mathsf{CO}_{3}, \mathsf{DMF} \\ & & & \\ \mathsf{MW} \ (40 \text{ W}, \ 130 \ {}^{\circ}\mathsf{C}), \ 20 \text{ min} \end{array} \overset{\mathsf{Ph}}{\underset{\mathsf{Ph}}{\overset{\mathsf{Ph}}{\underset{\mathsf{2a}}}} \begin{array}{c} \mathsf{Ar} \\ \mathsf{Ph} \\ \mathsf{2a} \ (\beta) \\ \mathsf{Ar} = 4 \text{-}\mathsf{MeOC}_{6}\mathsf{H}_{4} \end{array}$ 

Entry	Х	Pd cat.	$\mathbf{R}^{1}\mathbf{R}^{2}_{2}$	Yield [%] <sup>[a]</sup>	β/α <sup>[b]</sup>
1	(OH) <sub>2</sub>	1b	$(t-Bu)_3$	85	83/17
2	$(OH)_2$	1b	Cp <sub>3</sub>	22	99/1
3	$(OH)_2$	1b	$(n-Bu)_3$	45	99/1
4	$(OH)_2$	1b	$(i-Pr)_3$	46	99/1
5	$(OH)_2$	1b	$Me(t-Bu)_2$	25	99/1
6	$(OH)_2$	<b>1</b> a	(t-Bu) <sub>3</sub>	9	98/2
7	$(OH)_2$	_[c]	$(t-Bu)_3$	34	88/12
8	$(OH)_2$	_[d]	$(t-Bu)_3$	48	86/14
9	$(OH)_2$	_[e]	$(t-Bu)_3$	54	85/15
10	$[OC(Me_2)]_2$	1b	$(t-Bu)_3$	57	99/1
11	$F_{3}K$	1b	$(t-Bu)_3$	67	92/8
12	(OCOCH <sub>2</sub> ) <sub>2</sub> NMe	1b	$(t-Bu)_3$	<5	_

<sup>[a]</sup> Isolated yield after flash chromatography.

<sup>[b]</sup> Determined by GC analysis over the crude reaction mixture.

<sup>[c]</sup> Pd(OAc)<sub>2</sub> (0.1 mol% Pd) was used as catalyst.

<sup>[d]</sup> PdCl<sub>2</sub> (0.1 mol% Pd) was used as catalyst.

[e] Pd<sub>2</sub>(dba)<sub>3</sub> (0.1 mol% Pd) was used as catalyst.

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_ ^>	ArCI + $B(OH)_2$ $(0.1 \text{ m}) = (HP(t-Bu)_3)BF$ TBAOH (2 K_2CO_3	1b (0.1 mol% Pd) [HP( <i>t</i> -Bu) <sub>3</sub> ]BF₄ (0.2 mol%) TBAOH (20 mol%) K <sub>2</sub> CO <sub>3</sub> , DMF		Ar	
R	✓ MW (40 Ŵ, 13	0 °C), 20 min	R 2	3	
Entry	Product	No.	Yield [%] <sup>[a]</sup>	2/3 <sup>[b]</sup>	
1	MeO Ph	2a	85	87/13	
2	Me	2b	75	87/13	
3	Me Ph	2c	94	78/22	
4	Me Ph Me Me	2d	60	94/6	
5	Ph	2e	78 <sup>[c]</sup>	95/5	
6 7	X Ph	2f (X = OH) 2g (X = NH <sub>2</sub> )	94 <sup>[c]</sup> 70 <sup>[d]</sup>	90/10 91/9	
8	MeO	2h	58 <sup>[e]</sup>	-	
9	MeO	l <sub>11</sub> 2i	72 <sup>[c]</sup>	76/24	
10	Me n-C <sub>5</sub> H <sub>11</sub>	2j	71	88/12	
11		2k	73 <sup>[e]</sup>	88/12	
12	N Ph	21	94	>99/1	
13	S Ph	2m	95	90/10	
14		2n	84	>99/1	
15	S n-C <sub>8</sub> H <sub>17</sub>	20	31 <sup>[e]</sup>	>99/1	
16	N n-C4H	2p 1 <sub>9</sub>	33 <sup>[f]</sup>	>99/1	

Table 2. Suzuki alkenylation of aryl chlorides.

<sup>[a]</sup> Isolated yield for **2** and **3** after flash chromatography.

<sup>[b]</sup> Determined by GC on the crude reaction.

<sup>[c]</sup> 0.5 mol% Pd and 1 mol% of  $[HP(tBu)_3]BF_4$  were used.

- <sup>[d]</sup> Reaction time: 40 min. Isolated as acetamide.
- <sup>[e]</sup> The potassium trifluoroborate derivative was used as boron source.
- <sup>[f]</sup> The pinacol boronic ester derivative was used as boron source.

lectivity was observed when coupling 4-chloroanisole and 4-chlorotoluene with trans-2-phenylvinylboronic acid (Table 2, entries 1 and 2). 3,4-Dimethylchlorobenzene was coupled with *trans*-2-phenylvinylboronic acid in an excellent 94% isolated yield in the presence of 0.25 mol% of palladacycle 1b, giving the corresponding product with a good  $\beta/\alpha$  regioselectivity (78/ 22) (Table 2, entry 3). The regioselectivity of the process was higher when using sterically hindered aryl chlorides as demonstrated with the coupling of 2chlorotoluene and 2,6-dimethylchlorotoluene (Table 2, entries 4 and 5), as well as when 4-chlorophenol and 4-chloroaniline were used as electrophiles (entries 6 and 7). As depicted in entry 8 for the coupling of 3,5-dimethoxychlorobenzene, a successful vinylation reaction required the employment of potassium vinyltrifluoroborate as nucleophile,<sup>[18]</sup> affording compound 2h in a 58% isolated yield. Good yields (71-73%) were also observed when *trans*-1-hepten-1ylboronic acid and potassium trans-1-decen-1-yltrifluoroborate were employed as nucleophiles although, regardless of the boron source employed, in moderate regioselectivities, as depicted in Table 2, entries 9-11 for the coupling of 4-chloroanisole, 2,6-dimethylchlorobenzene, and 1-chloronaphthalene.

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In order to test the effectiveness of the catalytic system with heterocyclic chlorides, 2-chloropyridine, 2-chlorothiophene, and 2-chloroquinoline were submitted to the coupling with trans-2-phenylvinylboronic acid under the optimized reaction conditions. As shown in Table 2, entries 12–14, all three chlorides stereospecifically afforded the corresponding adducts **2l–2n** in excellent yields (84–95%) and very high  $\beta/\alpha$ regioselectivities (up to >99/1). Lower yields were observed when the heterocyclic chlorides were crosscoupled with  $\beta$ -alkyl-substituted alkenylboron nucleophiles as depicted in Table 2 entries 15 and 16, for the coupling of 2-chlorothiophene and 2-chloroquinoline with potassium trans-1-decen-1-yltrifluoroborate and trans-1-hexen-1-ylboronic acid pinacol ester, which afforded regioselectively compounds 20 and 2p in 31 and 33% yield, respectively.

We next extended the substrate scope to allyl and benzyl chlorides (Table 3). Oxime palladacycle **1b** (0.1 mol% Pd) in the presence of  $[HP(t-Bu)_3]BF_4$ (0.2 mol%) showed high catalytic activity towards the alkenylation of allyl chlorides affording the corresponding cross-coupled products **4** in high yields (63 to 95%) (Table 3, entries 1–6). As shown in entries 1– 4, (*E*)-(3-chloroprop-1-en-1-yl)benzene reacted with alkenylboronic acids and potassium alkenyltrifluoroborates to give the corresponding 1,4-dienes in excellent yields (91–95%), regio- and diastereoselectivities with the exception of the vinylation reaction with potassium vinyltrifluoroborate, that yielded compound **4b** in a 63% isolated yield (Table 3, entry 2). In the case of using crotyl chloride<sup>[19]</sup> as electrophile, good **Table 3.** Suzuki cross-coupling reactions of allyl- and benzyl chlorides.



<sup>[a]</sup> Isolated yield after flash chromatography.

<sup>[a]</sup> Z/E: 40/60.

- <sup>[c]</sup> A 3% (GC conversion) of (*E*)-(3-methylpenta-1,4-dien-1-yl)benzene (**5e**) was also observed.
- <sup>[d]</sup> Z/E: 16/84.
- [e] An 8% (GC conversion) of 1-(but-3-en-2-yl)naphthalene (5f) was also obtained.

yields were also obtained in the coupling with *trans*-2phenylvinylboronic acid (entry 5) and naphthalen-1ylboronic acid (entry 6), detecting some double bond isomerization in the former case. Regarding regioselectivity, small amounts of the regioisomers 5e and 5f were also identified.<sup>[19]</sup>

With respect to benzylic chlorides, 1-(chloromethyl)-4-vinylbenzene reacted with boronic acids and potassium trifluoroborates yielding the corresponding cross-coupled products **6** in good yields (Table 3, entries 7–9). Thus, reaction with *trans*-2-phenylvinylboronic acid afforded compound **6a** in 86% isolated yield (entry 7). On the other hand, a good 63% isolated yield was obtained when coupling with potassium vinyltrifluoroborate (Table 3, entry 8), and an 86% yield of compound **6c** was achieved when using potassium *trans*-1-decen-1-yltrifluoroborate as nucleophile (Table 3, entry 9).

In summary, the catalyst formed *in situ* from readily available and easily handled oxime palladacycle **1b** and tris(*tert*-butyl)phosphonium tetrafluoroborate, shows very good activity in the Suzuki coupling of a wide range of organic chlorides with alkenylboronic acids or potassium alkenyltrifluoroborates under MW irradiation conditions employing TBAOH as cocatalyst and DMF as solvent. Further studies addressing the extension of this catalytic system to other palladium-catalyzed transformations are currently underway.

### **Experimental Section**

# Typical Procedure for the Suzuki Coupling under MW Irradiation Conditions

A fresh stock solution of catalyst 1b (30 µg, 0.0075 mmol) in DMF (2.5 mL) and [HP(t-Bu)<sub>3</sub>]BF<sub>4</sub> (40 µg, 0.0375 mmol) in DMF (2.5 mL) were prepared. A 10-mL microwave vessel was charged with  $K_2CO_3$  (1.5 mmol, 207 mg), TBAOH 120 mg), *trans*-2-phenyvinylboronic (0.15 mmol. acid (1.12 mmol, 166 mg), catalyst 1 (250 µL of the stock solution, 0.00075 mmol, 3 µg, 0.1 mol% Pd), [HP(t-Bu)<sub>3</sub>]BF<sub>4</sub> (250 µL of the stock solution, 0.00375 mmol, 4 µg), 4-chloroanisole (0.75 mmol, 92 µL), and DMF (1.5 mL). The vessel was sealed with a pressure lock and the mixture was heated in air at 130°C by MW irradiation of 40 W for 20 min in a CEM Discover MW reactor. After allowing the reaction mixture to cool down to room temperature, it was filtered through a pad of celite and poured into an excess of water (5 mL) and extracted with Et<sub>2</sub>O ( $3 \times 5$  mL). The combined organic phases were washed with water  $(3 \times 5 \text{ mL})$ , dried (MgSO<sub>4</sub>), and evaporated. The obtained crude material was purified by flash chromatography (hexane/AcOEt: 95/5). The pure compound (E)-4-methoxystilbene (2a) was obtained as a white solid; yield. 85%; mp 135°C (hexane); R<sub>f</sub> 0.12 (hexane). IR (KBr): v=3387, 2958, 2924, 2878, 2859, 1459, 1378, 1067 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta =$ 7.51–7.44 (m, 4H), 7.37–7.32 (t, 2H, J=7.34 Hz), 7.26–7.23 (t, 1H, J=6.1 Hz), 7.08, 6.96 (2d, 2H, J=16.4 Hz), 6.89 (d, J=16.4 Hz)2H, J=8.9 Hz), 3.83 (s, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):  $\delta = 159.3, 137.6, 130.1, 128.6, 128.2, 127.7, 127.2, 126.6, 126.2,$ 114.1, 55.3; MS: m/z (%)=211 ( $M^+$ +1, 18%), 210 ( $M^+$ , 100), 209  $(M^+-1, 16)$ , 195 (16), 167 (29), 166 (16), 165 (42), 151 (28), 136 (14), 134 (23), 105 (10), 104 (16), 76 (19), 62 (11), 50 (12).

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