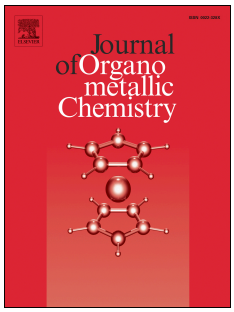


4-Amino-1,2,4-triazoles and 1,3,4-oxadiazoles·palladium(II) recoverable complexes as catalysts in the sustainable Suzuki-Miyaura cross-coupling reaction

Manel Chehrouri, Cristina Moreno-Cabrerizo, Adil A. Othman, Ihssene Chabour, Marcos Ferrándiz-Saperas, Inmaculada Sempere, H. Ali Döndaş, M. de Gracia Retamosa, José M. Sansano

PII: S0022-328X(20)30255-2

DOI: https://doi.org/10.1016/j.jorganchem.2020.121353

Reference: JOM 121353

To appear in: *Journal of Organometallic Chemistry*

Received Date: 5 April 2020

Revised Date: 22 May 2020

Accepted Date: 24 May 2020

Please cite this article as: M. Chehrouri, C. Moreno-Cabrerizo, A.A. Othman, I. Chabour, M. Ferrándiz-Saperas, I. Sempere, H.A. Döndaş, M. de Gracia Retamosa, José.M. Sansano, 4-Amino-1,2,4-triazoles and 1,3,4-oxadiazoles·palladium(II) recoverable complexes as catalysts in the sustainable Suzuki-Miyaura cross-coupling reaction, *Journal of Organometallic Chemistry* (2020), doi: https://doi.org/10.1016/j.jorganchem.2020.121353.

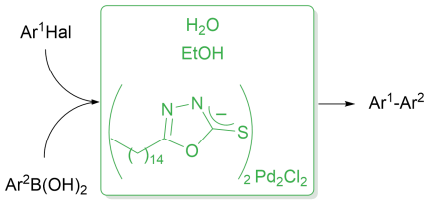
Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

4-Amino-1,2,4-triazoles and 1,3,4-oxadiazoles·Palladium(II) recoverable complexes as catalysts in the sustainable Suzuki-Miyaura cross-coupling reaction

Leave this area blank for abstract info.

Manel Chehrouri, Cristina Moreno-Cabrerizo, Adil A. Othman, Ihssene Chabour, Marcos Ferrándiz-Saperas, Inmaculada Sempere, H. Ali Dondas, M. de Gracia Retamosa and José M. Sansano.



Journal of Organometallic Chemistry
journal homepage: www.elsevier.com

4-Amino-1,2,4-triazoles and 1,3,4-oxadiazoles·palladium(II) recoverable complexes as catalysts in the sustainable Suzuki-Miyaura cross-coupling reaction

Manel Chehrouri,[a] Cristina Moreno-Cabrerizo,[b] Adil A. Othman,[a]* Ihssene Chabour,[b] Marcos Ferrándiz-Saperas,[b] Inmaculada Sempere,[b] H. Ali Döndaş,[c] M. de Gracia Retamosa[d] and José M. Sansano[b]*

[a] *Laboratoire de Synthèse Organique Bioactive, Département de Chimie Physique, Faculté de Chimie, Université des Sciences et de la Technologie d'Oran, Mohamed Boudiaf-USTO-MB, BP. 1505, El-M'naouer, 31003 Oran, Algeria*
[b] *Departamento de Química Orgánica, Instituto de Síntesis Orgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Universidad de Alicante 03080-Alicante, Spain.*
[c] *Department of Chemistry, Faculty of Pharmacy, Mersin University, Yenisehir, 33169, Mersin, Turkey.*
[d] *Universidad de Sevilla and Centro de Innovación en Química Avanzada (ORFEO-CINQA) Avda. Américo Vespucio, 49,41092 Sevilla (Spain).*
** indicates the main/corresponding author, adelaliothman@gmail.com, jmsansano@ua.es*

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
palladium
micellar
water/ethanol
recycling
Suzuki-Miyaura

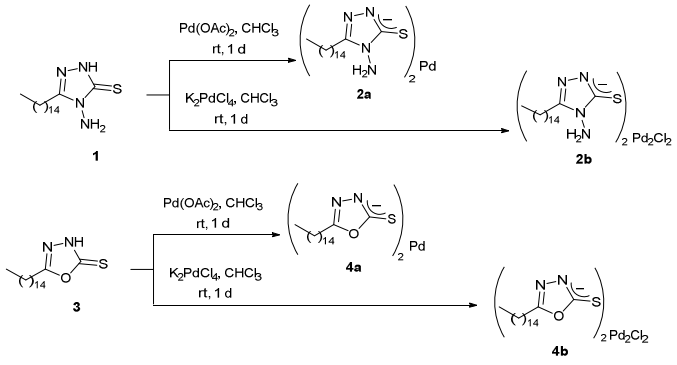
ABSTRACT

The Suzuki-Miyaura cross-coupling reaction using 4-amino-1,2,4-triazoles and 1,3,4-oxadiazoles·palladium(II) is studied. The reaction is optimized and the most appropriate catalytic complex is tested with several aryl halides, boronic acids in an environmentally benign solvent system (H_2O/ EtOH). The recovery of the catalytic species is also surveyed because of the nature of the employed solvent. A domino process is efficiently carried out following the standard conditions. Several surface parameters of the ligands are analyzed and the resulting values are extrapolated to the insoluble palladium catalyst.

1. Introduction

The Suzuki-Miyaura cross-coupling reaction is one of the most useful and versatile ways to achieve different series of compounds (preferentially biaryls) where a new Csp^2-Csp^2 bond is formed.[1-20] The resulting molecules derived from this transformation have different applications in many areas. For example, in the preparation of natural products, nucleoside surrogates, drugs, liquid crystals and pharmaceutically interesting compounds.[21-23] A large number of reports concerning the Suzuki-Miyaura coupling reactions appeared showing improvements. For example, conducting the Suzuki-Miyaura coupling reaction in environmentally friendly solvents such as water or alcohols have particular importance.[24-42] In this sense, the importance of the nature of the ligands of the palladium complex determine the availability to run couplings to perform a later recovery or reuse of them in this media. The employment of ligands with surfactant nature,[43] coordinated to the palladium atom, is crucial to recycle the catalytic system and is not very frequent in organic chemistry.[44] The most studied approach is the use of additives with micellar/surfactant character facilitating this coupling reaction in water or aqueous systems.[45]

We have studied the already described long-chain attached to heterocyclic scaffolds **1** and **3**, derived from palmitic acid,[46] to generate palladium(II) complexes **2** and **4** (Scheme 1) using different metallic sources. These species, specially **2a** and **2b** were efficient in conventional examples of both Tsuji-Trost and Mizoroki-Heck reactions, in acetonitrile and toluene, respectively.[47]



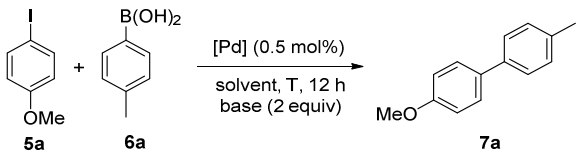
Scheme 1. Synthesis of palladium complexes **2** and **4**.

The potential amphiphilic properties of entities **2** and **4** envisage the success of reactions run in aqueous media. So, in this work, the ability of these complexes to operate in Suzuki-Miyaura cross-couplings, performed in aqueous solutions, is studied. This character would also permit to recover the catalyst and reuse it with total efficiency.

2. Results and Discussion

Initially, the preparation of known heterocyclic ligands **1** and **3** was performed, according to the literature, starting from palmitic acid.[47] Next, the preparation of the palladium(II) complexes **2** and **4** was done according to the procedure depicted in Scheme 1. We proposed these tentative structures on the basis of elemental analysis, and various instrumental techniques, since it was not possible to isolate an appropriate crystal to run X-ray diffraction analysis.[46,47] The optimization of the benchmark Suzuki-Miyaura cross-coupling between iodoanisol and *p*-tolylboronic acid was done using conditions reported in the literature with heterocyclic palladium(II) complexes.[48] Looking for an environmental friendly process, EtOH was selected as solvent and KOH as base at 78 ºC. The four complexes afforded very good conversions (Table 1, entries 1-4) being selected **4b** because the reaction crude was very clean (^{1}H NMR) and traces of the homocoupled product were not detected. The reaction in neat water was not complete after 12 h (Table 1, entry 5). However, the combination of water/ethanol in equal proportions afforded an excellent conversion and very clean reaction product **7a** (Table 1, entry 6) in a bath at 100 ºC. The employment of potassium carbonate as base or assaying lower catalyst loading (0.25 mol%) gave the final coupling product in 95 and 55% conversion (this reaction was not completed after 12 h), respectively (Table 1, entries 7 and 8).

Table 1. Optimization of the Suzuki-Miyaura cross-coupling between iodoanisol and *p*-tolylboronic acid.



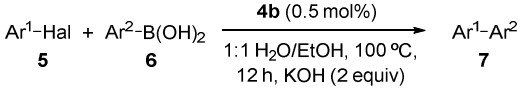
5a **6a** **7a**

Ent.	[Pd]	Solvent	Base	T (ºC)	Conv. (%)[a,b]
1	**2a**	EtOH	KOH	78	98
2	**2b**	EtOH	KOH	78	83
3	**4a**	EtOH	KOH	78	99
4	**4b**	EtOH	KOH	78	96
5	**4b**	H_2O	KOH	100	20
6	**4b**	H_2O/EtOH	KOH	100	99
7	**4b**	H_2O/EtOH	K_2CO_3	100	95
8	**4b**[c]	H_2O/EtOH	KOH	100	55

[a] Reaction conditions: **5a** and **6a** (0.2 mmol each), base (0.4 mmol), [Pd] (0.5 mol%), solvent (2 mL), 12 h at the bath temperature indicated.
[b] Isolated crude conversions determined by gas chromatography.
[c] 0.25 mol% of **4b** was employed.

With the more suitable conditions, and inside of a pressure tube, the scope of the reaction was surveyed (Table 2). Aryl iodides **5** reacted with arylboronic acids **6** affording excellent yields of biaryls **7** using a bath of 100 ºC for 12 h (Table 2, entries 1-15). Apparently, there is no important effects of the substituents in the final yield of products **7**. Both electron-donating and electron-withdrawing groups can be used. Also, heterocyclic components are appropriate to run this reaction (Table 2, entries 8 and 9). Aryl bromides needed a 120 ºC bath to promote the reaction successfully in very high yields too (Table 2, entries 16-23). However, the reaction of aryl chlorides is very slow and despite increasing the temperature up to 150-160 ºC (bath) very small conversions were obtained. These results allowed the total chemoselective transformation in 4-iodochlorobenzene and 4-chlorobromobenzene (Table 2, entries 15 and 20). In addition, nonsteroidal anti-inflammatory drug (Felbinac, **7s**) was prepared and isolated in 90% yield in a 2 mmol scale.

Table 2. Pd-Catalyzed allylation of 3-acetyl-2-oxindoles



5 **6** **7**

Ent.	Hal	Ar^1	Ar^2	**7**	Yield (%)[a,b]
1	I	4-(MeO)C_6H_4	4-MeC_6H_4	**7a**	96
2	I	4-(MeO)C_6H_4	4-(CF_3)C_6H_4	**7b**	89
3	I	4-(MeO)C_6H_4	4-(CHO)C_6H_4	**7c**	91
4	I	4-(MeO)C_6H_4	4-FC_6H_4	**7d**	93
5	I	4-(MeO)C_6H_4	2-(BnO)C_6H_4	**7e**	89
6	I	4-(MeO)C_6H_4	Ph	**7f**	91
7	I	3-(MeO)C_6H_4	4-MeC_6H_4	**7g**	88
8	I	2-Pyridyl	4-MeC_6H_4	**7h**	91
9	I	2-Thienyl	4-MeC_6H_4	**7i**	85
10	I	2-Naphthyl	4-MeC_6H_4	**7j**	84
11	I	4-MeC_6H_4	4-MeC_6H_4	**7k**	92
12	I	Ph	Ph	**7l**	92
13	I	4-MeC_6H_4	Ph	**7m**	89
14	I	4-FC_6H_4	Ph	**7n**	89
15	I	4-ClC_6H_4	Ph	**7o**	88
16	Br[c]	4-(MeO)C_6H_4	Ph	**7f**	77
17	Br[c]	4-(CN)C_6H_4	Ph	**7p**	85
18	Br[c]	4-(CHO)C_6H_4	Ph	**7q**	90
19	Br[c]	4-(NO_2)C_6H_4	Ph	**7r**	92
20	Br[c]	4-ClC_6H_4	Ph	**7o**	90
21	Br[c]	4-(MeO)C_6H_4	4-MeC_6H_4	**7a**	89
22	Br[c]	2-Naphthyl	4-MeC_6H_4	**7j**	86
23	Br[c]	4-(CH_2CO_2H)C_6H_4	Ph	**7s**	92[d]

[a] Reaction conditions: **5** (0.2 mmol), boronic acid (0.2 mmol), **4b** (0.5 mol%), KOH (0.4 mmol), 1:1 water/EtOH (2 mL), pressure tube at 100 ºC (bath temperature) 12 h.
[b] Isolated yield after flash chromatography.
[c] Reaction performed at 120 ºC (bath temperature).
[d] Performed in 2 mmol scale.

With the aim of recovering the catalyst, taking advantage of the suspension/dispersion of the catalytic species in water, the ethanol was evaporated after completing the first batch of the coupling of *p*-iodoanisole. Then, ethyl acetate was added extracting the product **7a**. The aqueous suspension was again submitted to a new process giving high chemical yields. The procedure was repeated up to the fifth recycled experiment arising very high yield of **7a** (Figure 1). We stopped the study in this point, but we are sure that it is possible to run another 5 catalytic cycles more with the same catalyst. The catalyst demonstrated to be very stable and did not lost its catalytic efficiency. A new cross-coupling reaction was performed using the aqueous phase resulting from the first cycle, previously filtered, and an extremely low conversion (<10%) was obtained. This result indicated the heterogeneous character of this catalysis. The estimated TON is very close to 200 and the TOF is 16.7 h^{-1}. This study was also repeated twice in the preparation and isolation, by precipitation in acidic media, of drug **7s**, affording this product in 89% yield after the second catalytic bath.

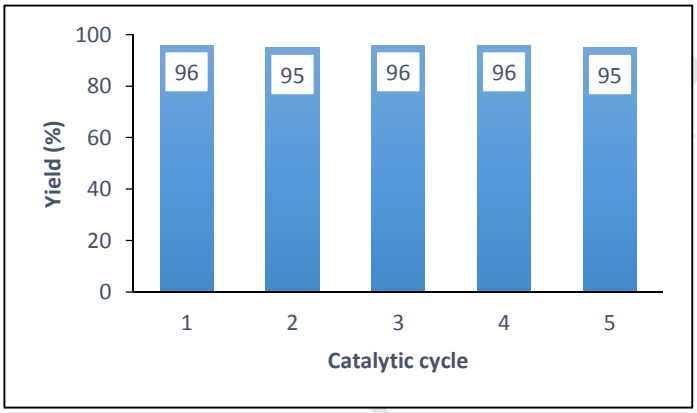
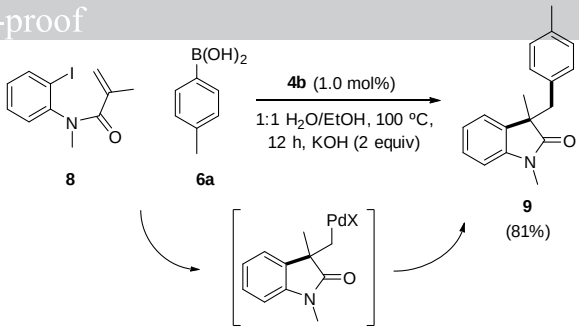


Figure 1. Synthesis of compound **7a** using the same recycled catalyst.

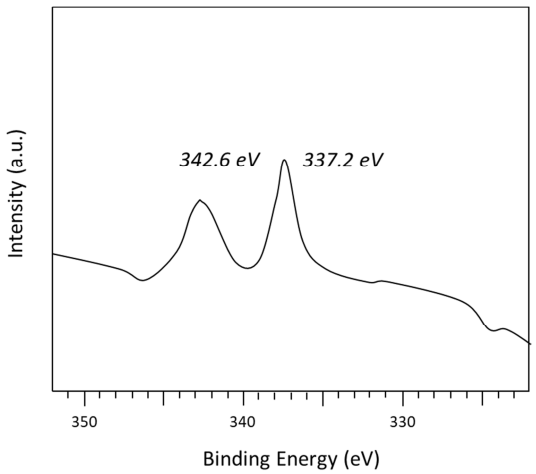
The catalyst **4b** was also submitted to a domino process involving an intramolecular Mizoroki-Heck type reaction in **8**. Here, the alkene acted as internal relay system, which inhibited the β-hydride elimination of the intermediate organometallic species, after the 5-*exo*-*trig*-cyclization step.[49,50] The resulting palladium-Csp^3 intermediate finally underwent the expected Suzuki-Miyaura cross-coupling with *p*-tolylboronic acid. This sequential double Csp^2-Csp^3 formation occurred in the presence of 1 mol% of the catalyst in 81% yield (Scheme 2). Again, the catalyst could be recovered from the aqueous suspension and reused in another new reaction affording the same result.



Scheme 2. Synthesis of product **9** through a domino sequence.

The nature of palladium complex **4b** was a brown sticky dense oil. After finishing a catalytic cycle, the catalyst was filtered of and a similar aspect was observed. If a new catalytic cycle is attempted with this filtered solution the reaction did not occur, so this ensures the heterogeneous character of this catalysis. The presence of nanoparticles was very difficult to observe after analysis of TEM. We studied the XPS results of the catalyst before and after the Suzuki-Miyaura cross-coupling concluding that the reduction of palladium(II) to zero-valent palladium occurred during the chemical process (Figure 2). Although the mercury test is a rapid and accepted used method for identifying homogeneous molecular catalysis from nanoparticle metal catalysis, it has been published that this test is generally inadequate under certain conditions.[51] The mixture of the freshly prepared complex in the first catalytic cycle for the synthesis of compound **7a** was treated with 100 equiv of mercury for 1 d at 100 ºC (300 rpm, magnetic stirrer rotation rate) and the observed conversion decreased to 58%. Besides, when the same poisoning conditions were applied to the reaction performed using the recovered catalytic complex (for example, second cycle of Figure 1) the Suzuki-Miyaura coupling occurred only in a 15% conversion. At this point, the presence of palladium nanoparticles could be confirmed but operating in an heterogeneous mode. According to all these facts and the literature precedents, a plausible mechanistic formation of these nanoparticles can be draw (Scheme 3).[44a]

a)



b)

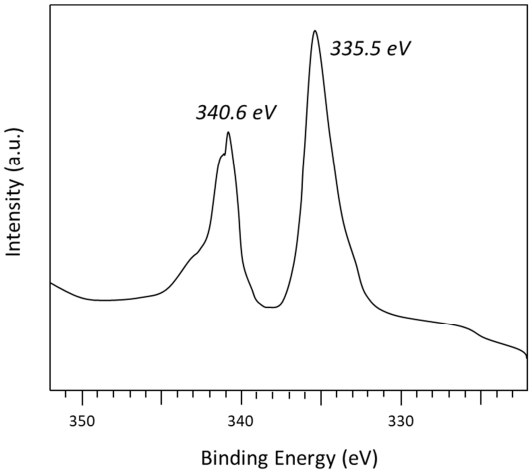
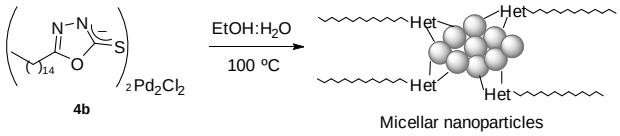


Figure 2. XPS of **4b** (a), and XPS of the catalyst filtered after the reaction (b).



Scheme 3. Plausible formation of micellar nanoparticles.

The evaluation of same surface properties of palladium complexes **2** and **4** were very difficult due to their scarce solubility in organic solvents. However, a closer information can be obtained by the assessment of these properties of the heterocyclic ligands **1** and **3**. Critical micelle concentration (CMC) values were determined plotting the electrical conductivity of the solutions in chloroform *versus* the concentration (M) (Table 3).[52] The two values are in the same range and corresponded to classical non-ionic surfactants.[52,53] The micellization free energy was calculated from the CMC value (ΔG^{o}_{mic} = 2.303·R·T·log CMC).[52] The similar results obtained for both samples confirmed the spontaneous micellization processes. Measurements of the hydrophilic lipophilic balance (HLB) using Griffin's equation[54] provided parameters of 7.05 and 6.47 (Table 3). These values predict that the ligands **1** and **3** can be classified as wetting/spreading agent and water in oil emulsifying agent, respectively, but both of them are water dispersible substances.[55] By extrapolation of these results towards the catalyst **4b**, the CMC value would be higher than the corresponding ligand due to its more ionic character, and, in consequence the negative micellization free energy would ensure a spontaneous micellization. In addition, it would be expected a HLB ~ 10 value, affording a water dispersion and oil in water emulsifying agent.

Table 3. Determination of surface properties of ligands **1** and **3**.

Ligand	CMC[a]	ΔG^{o}_{mic}[b]	HLB[c]	Classification[d]
1	9.0	-23.10	7.05	Water dispersible Wetting/spreading agent
3	7.8	-23.45	6.47	Water dispersible Water in oil emulsifying agents

[a] Measured in chloroform, $x10^{-5}$ (M).
[b] In kJ·mol^{-1}.
[c] Calculated from Griffin's equation.
[d] Established according to HLB values.[55]

3. Conclusions

The efficiency of the palladium complex **4b** in the Suzuki-Miyaura cross-coupling reaction, with surfactant character, was demonstrated. Unfortunately, aryl chlorides were not appropriate substrates for this catalytic complex. The required mild conditions and the recycling of the catalytic species were important parameters to consider. The surface properties could be extrapolated from measurements done to the heterocyclic precursor. The robustness of this catalytic system was evaluated by the successful domino reaction performed. In comparison with analogous systems operating in water or aqueous solvents, the results are in the same ranges as depicted in Table 4. The most important feature of this catalytic complex is the high percentage during the recovery and its ability to run a new process with the same efficiency (>5 cycles).

Table 4. Comparison between the results of this work with the other ones published previously.[a]

Ref.	[Pd] (mol%)	time	T (ºC)	HalAr	Catal. cycles
[44a]	0.1	24 h	80	Br	5
[44b]	0.5	30 min	100	Br, I	10
[44c]	0.5	4 h	50	Br, I	nr[b]
[44d]	0.1-2.0	2-22 h	rt-100	Cl	nr[b]
[44e]	0.005	24	100	Br, I	10
[44f]	0.1	2.5-4.5 h	50	Cl, Br, I	5
[44g]	0.1	5 min[c]	100	Br	nr[b]
[44h]	0.05	2 h	85	Br	nr[b]
[44i]	0.5	24 h	100	Cl	nr[b]
[44j]	0.1	12 h	rt	Cl, Br, I	nr[b]
[44k]	0.5	6 h	80	Cl, Br	nr[b]
[44l]	0.06	1-24 h	45	Br, I	8
[44m]	0.01	0.5-10 h	70	Cl, Br, I	8
[44n]	1-5	5	60	Cl, Br, I	5
[42]	0.2	24	80-120	Cl, Br, I	6
[d]	0.5	12	100	Br, I	>5

[a] All data are referred for a similar chemical yield.
[b] nr: no reported.
[c] Under microwaves irradiation.
[d] This work.

4. Experimental section

4.1 General information.

All commercially available reagents and solvents were used without further purification, only aldehydes were also distilled prior to use. Analytical TLC was performed on Schleicher & Schuell F1400/LS 254 silica gel plates, and the spots were visualized under UV light (l ¼ 254 nm). Flash chromatography was carried out on hand-packed columns of Merck silica gel 60 (0.040-0.063 mm). The structurally most important peaks of the IR spectra (recorded using a Nicolet 510 PFT) are listed and

wave numbers are given in cm^{-1}. NMR spectra were obtained using a Bruker AC-300 or AC-400 and were recorded at 300 or 400 MHz for ^{1}H NMR and 75 or 100 MHz for ^{13}C NMR, using $CDCl_3$ as solvent and TMS as internal standard (0.00 ppm). The following abbreviations are used to describe peak patterns where appropriate: s singlet, d doublet, t triplet, q quartet, m multiplet or unresolved and br s broad signal. All coupling constants (*J*) are given in Hz and chemical shifts in ppm. ^{13}C NMR spectra were referenced to $CDCl_3$ at 77.16 ppm. DEPT-135 experiments were performed to assign CH, CH_2 and CH_3. Low resolution electron impact (EI) mass spectra were obtained at 70 eV using a Shimadzu QP-5000 by injection or DIP; fragment ions in m/z are given with relative intensities (%) in parentheses. High resolution mass spectra (HRMS) were measured on an instrument using a quadrupole time-of-flight mass spectrometer (QTOF) and also through the electron impact mode (EI) at 70 eV using a Finnigan VG Platform or a Finnigan MAT 95 S.

*4.2. General procedure for the preparation of known compounds **7**.*

To a solution of the aryl iodide or bromide (0.2 mmol) and the corresponding boronic acid (0.2 mmol) in a 1:1 water:EtOH mixture (2 mL), complex **4b** (1 mg, 0.5 mol%) and KOH (11.5 mg, 0.4 mmol) were added and the resulting suspension was stirred at 100 ºC (oil bath) for 12 h. Then ethanol was evaporated (under vacuo) and the aqueous solution extracted with ethyl acetate (3x5 mL). The combined organic phases were dried ($MgSO_4$) filtered and evaporated. The resulting crude material was purified by flash chromatography (*n*-hexane:ethyl acetate).

For the recycling series, once the reaction finished, ethanol was evaporated (under vacuo) and the water suspension extracted with ethyl acetate (3x5 mL). The combined organic portions were treated as above, whilst the aqueous suspension was combined with another batch of the aryl iodide and boronic acid dissolved (0.2 mmol each) in ethanol (1 mL).

4-Methoxy-4'-methyl-1,1'-biphenyl (**7a**).[56]
4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (**7b**).[57]
4'-Methoxy-[1,1'-biphenyl]-4-carbaldehyde (**7c**).[58]
4-Fluoro-4'-methoxy-1,1'-biphenyl (**7d**).[59]
2-(Benzyloxy)-4'-methoxy-1,1'-biphenyl (**7e**).[60]
4-Methoxy-1,1'-biphenyl (**7f**).[61]
3-Methoxy-4'-methyl-1,1'-biphenyl (**7g**).[62]
3-(*p*-Tolyl)pyridine (**7h**).[63]
2-(*p*-Tolyl)thiophene (**7i**).[58]
1-(*p*-Tolyl)naphthalene (**7j**).[58]
4,4'-Dimethyl-1,1'-biphenyl (**7k**).[64]
1,1'-Biphenyl (**7l**).[61]
4-Methoxy-1,1'-biphenyl (**7m**).[59]
4-Fluoro-1,1'-biphenyl (**7n**).[65]
4-Chloro-1,1'-biphenyl (**7o**).[66]
[1,1'-Biphenyl]-4-carbonitrile (**7p**).[67]
Biphenyl-4-carbaldehyde (**7q**).[68]
4-Nitro-1,1'-biphenyl (**7r**).[69]
2-[(1,1'-Biphenyl)-4-yl]acetic acid (**7s**).[70]
1,3-Dimethyl-3-(4-methylbenzyl)indolin-2-one (**9**).[71]

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge financial support from the Spanish Ministerio de Ciencia, Innovación y Universidades (projects CTQ2016-76782-P, CTQ2016-81797-REDC CTQ2016-81893REDT, and RED2018-102387-T) the Spanish Ministerio de Economía, Industria y Competitividad, Agencia Estatal de Investigación (AEI) and Fondo Europeo de Desarrollo Regional (FEDER, EU) (projects CTQ2016-76782-P), the Generalitat Valenciana (PROMETEOII/2014/017), USTO-MB and the Universities of Mersin and Alicante. One of us (M.C.) thanks USTO-MB for scientific leave.

References

1 J. Buchspies, M. Szostak, *Catalysts* 9 (2019) 53.

2 S.E. Hooshmand, B. Heidari, R. Sedghi, R.S. Varma, *Green Chem*. 21 (2019) 381.

3 I.P. Beletskaya, F. Alonso, V. Tyurin, *Coord. Chem. Rev*. 385 (2019) 137.

4 L. González-Sebastián, D. Morales-Morales, *J. Organomet. Chem*. 893 (2019) 39.

5 A. Biffis, P. Centomo, A. Del Zotto, M. Zecca M, *Chem. Rev*. 118 (2018) 2249.

6 D. Roy, Y. Uozumi, *Adv. Synth. Catal*. 360 (2018) 602.

7 A.T.K. Koshvandi, M.M. Heravi, T. Momeni, *Appl. Organomet. Chem*. 32 (2018) 4210.

8 A. Chatterjee, T.R. Ward, *Catal. Lett*. 146 (2016) 820.

9 J. Sołoducho, K. Olech, A. Świst, D. Zając, J. Cabaj, *Adv. Chem. Engineer. Sci.* 3 (2013) 19.

10 M. Mora, C. Jiménez-Sanchidrián, J.R. Ruiz, *Curr. Org. Chem*. 16 (2012) 1128.

11 J. Magano, J.R. Dunetz, *Chem. Rev*. 111 (2011) 2177.

12 A. Suzuki, *Angew. Chem. Int. Ed*. 50 (2011) 6722.

13 N. Miyaura, in: Metal-Catalyzed Cross-Coupling Reactions, Wiley-VCH,Weinheim, 2008, pp. 41–123.

14 F. Alonso, I.P. Beletskaya, M. Yus, *Tetrahedron* 64 (2008) 3047.

15 N.T.S. Phan, M. van Der Sluys, C.W. Jones, *Adv. Synth. Catal*. 348 (2006) 609.

16 S. Kotha, K. Lahiri, D. Kashinath, *Tetrahedron* 58 (2002) 9633.

17 A. Kumar, G.K. Rao, S. Kumar, A.K. Singh, *Dalton Trans*. 42 (2013) 5200.

18 F. Bellina, A. Carpita, R. Rossi, *Synthesis* 15 (2004) 2419.

19 D.A. Alonso, C. Nájera, *Chem. Soc. Rev*. 39 (2010) 2891.

20 M. Gholinejad, Z. Naghshbandi, C. Nájera, *ChemCatChem* 11 (2019) 1792.

21 T. Willemse, W. Schepens, H.W.T. van Vlijmen, B.U.W. Maes, S. Ballet, *Catalysts* 7 (2017) 74.

22 N.K. Adlington, L.R. Agnew, A.D. Campbell, R.J. Cox, A. Dobson, C. Fernández-Barrat, M.A.Y. Gall, W. Hicks, G.P. Howell, A. Jawor-Baczynska, L. Miller-Potucka, M. Pilling, K. Shepherd, R. Tassone, B.A. Taylor, A. Williams, *J. Org. Chem*. 84 (2019) 4735.

23 H. Doucet, J.C. Hierso, *Curr. Opin. Drug Discov. Devel*. 10 (2007) 672.

24 H. Firouzabadi, N. Iranpoor, M. Gholinejad, *J. Organomet. Chem*. 695 (2010) 2093.

25 A. Kilic, E. Gezer, F. Durap, M. Aydemir, A. Baysal, *J. Organomet. Chem*. 896 (2019) 129.

26 S. Bunda, A. Udvardy, K. Voronova, F. Joó, *J. Org. Chem*. 83 (2018) 15486.

27 S. Dharani, G. Kalaiarasi, D. Sindhuja, V.M. Lynch, R. Shankar, R. Karvembu, R. Prabhakaran, *Inorg. Chem*. 58 (2019) 8045.

28 S. Doherty, J.G. Knight, T. Backhouse, E. Abood, H. Al-shaikh, A.R. Clemmet, N.J. Warren, *Adv. Synth. Catal*. 360 (2018) 3716.

29 A. Aktaş, D.B. Celepci, Y. Gök, M. Aygün, *Chemistry Select* 3 (2018) 10932.

30 S. Handa, F. Ibrahim, T.N. Ansari, F. Gallou, *ChemCatChem* 10 (2018) 4229.

31 K.S. Nayan, N. Satrawala, R.J. Kumar, *Eur. J. Inorg. Chem*. 16 (2018) 1743.

32 S. Xu, K. Song, T. Li, B. Tan, *J. Mater. Chem. A*. 3 (2015) 1272.

33 D. Sahu, A.R. Silva, P. Das, *Catal. Commun*. 86 (2016) 32.

34 N. Shahnaz, A. Puzari, B. Paul, P. Das, *Catal. Commun*. 86 (2016) 55.

35 F. Schroeter, J. Soellner, T. Strassner, *Organometallics* 37 (2018) 4267.

36 M. Kempasiddhaiah, V. Kandathil, R.B. Dateer, B.S.A. Patil, S.A. Patil, *Appl Organomet Chem*. 33 (2019) 4846.

37 S. Handa, M.P. Andersson, F. Gallou, J. Reilly, B.H. Lipshutz. *Angew. Chem. Int. Ed*. 55 (2016) 4914.

38 M. Gholinejad, F. Zareh, C. Nájera, *Appl. Organomet. Chem*. 32 (2018) 3984.

39 M. Gholinejad, M. Razeghi, C. Najera, *RSC Adv*. 5 (2015) 49568.

40 M. Gholinejad, M. Bahrami, C. Nájera, *Mol. Catal*. 433 (2017) 12.

41 J.D. Patil, S.N. Korade, S.A. Patil, D.S. Gaikwad, D.M. Pore, *RSC Adv*. 5 (2015) 79061.

42 F. Khosravi, M. Gholinejad, D. Lledó, G. Grindlay, C. Nájera, J.M. Sansano, *J. Organomet. Chem*. 901 (2019) 120941.

43 a) D. Lippincott, E. Landstrom, M. Cortés-Clerget, B.H. Lipshutz, K. Buescher, R. Schreiber, C. Durano, M. Parmentier, N. Ye, B. Wu, M. Shi, H. Yang, M. Andersson, F. Gallou, *Org. Process Res. Devel*. (2019), DOI:10.1021/acs.oprd.9b00454; b) A. Steven, *Synthesis* 51 (2019) 2632.

44 a) C. Wang, R. Ciganda, L. Salmon, D. Gregurec, J. Irigoyen, S. Moya, J. Ruiz, D. Astruc, *Angew. Chem. Int. Ed*. 55 (2016) 3091; b) V. Kairouz, A.R. Schmitzer, *Green Chem*. 16 (2014) 3117; c) H. Hattori, K-i. Fujita, T. Muraki, A. Sakaba, *Tetrahedron Lett*. 48 (2007) 6817; d) K.W. Anderson, S.L. Buchwald, *Angew. Chem. Int. Ed.* 44 (2005) 6173; e) Y.M.A. Yamada, *Chem. Pharm. Bull.* 53 (2005) 723; f) A.R. Hajipour, M.K. Tarrari, S. Jajarmi, *Appl. Organometal. Chem*. 32 (2018) e4171; g) J.I. Ortega-Gaxiola, H. Valdés, E. Rufino-Felipe, R.A. Toscano, D. Morales-Morales, *Inorg. Chim. Acta* 504 (2020) 119460; h) S. Yadav, A. Singh, N. Rashid, M. Ghotia, T.K. Roy, P.P. Ingole, S. Ray, S.M. Mobin, C. Dash, *ChemistrySelect* 3 (2018) 9469; i) F. Schroeter, J. Soellner, T. Strassner, *Organometallics* 37 (2018) 4267; j) D.

Sasidharan, C.V. Aji, P. Mathew, *Polyhedron* 157 (2019) 335; k) L. Fu, X. Cao, J.-P. Wan, Y. Liu, *Chin. J. Chem*. 38 (2020) 254; l) M. Niakan, Z. Asadi, M. Masteri-Farahani, *ChemistrySelect* 4 (2019) 1766; m) Y. Wang, Y. Liu, W.□q. Zhang, H. Sun, K. Zhang, Y. Jian, Q. Gu, G. Zhang, J. Li, Z. Gao, *ChemSusChem* 12 (2019) 5265; n) G. Dilauro, S. Mata-García, D. Tagarelli, P. Vitale, F.M. Perna, V. Capriati, *ChemSusChem* 11 (2018) 3495.

45 For recent examples, see: a) J.H. Hunter, L. Prendergast, L.F. Valente, A. Madin, G. Pairaudeau, M.J. Waring, *Bioconj. Chem*. 31 (2020) 149; b) A. Sanzone, S. Mattiello, G.M. Garavaglia, A.M. Calascibetta, C. Ceriani, M. Sassi, L. Beverina, *Green Chem*. 21 (2019) 4400; c) A.A. Adam, M. Szabados, A. Polyakovics, K. Musza, Z. Kanya, A. Kukovecz, P. Sipos, I. Palinko, *J. Nanosci. Nanotech*. 19 (2019) 453; d) D.S. Gaikwad, K.A. Undale, R.A. Kalel, D.B. Patil, *J. Iran. Chem. Soc*. 16 (2019) 2135; e) L. Liu, M. Liu, J. Yang, B. Zhu, X. Wang, *Curr. Org. Chem*. 22 (2018) 2023; f) C.E. Brocklehurst, F. Gallou, J. Hartwieg, D. Constanze, M. Palmieri, D. Rufle, *Org. Process Res. Devel*. 22 (2018) 1453; g) S. Handa, F. Ibrahim, T.N. Ansari, F. Gallou, *ChemCatChem* 10 (2018) 4229; h) A. Pourjavadi, Z. Habibi, *Appl. Organomet. Chem*. 32 (2018) 4480; i) P. Guo, H. Zhang, J. Zhou, F. Gallou, M. Parmentier, H. Wang, *J. Org. Chem*. 83 (2018) 7523; j) S. Fortun, A.R. Schmitzer, *ACS Omega* 3 (2018) 1889.

46 The preparation of homologous palladium complexes from oleic acid and its hydrogenated equivalent was reported. M. Chehrouri, A.A. Othman, C. Moreno‑Cabrerizo, M. Gholinejad, J.M. Sansano, *Monats. Chem.-Chem. Month*. 151 (2020) 173.

47 M. Chehrouri, A.A. Othman, S. Jiménez-Cecilia, C. Moreno-Cabrerizo, J.M. Sansano, *Synth. Commun*. 49 (2019) 1301.

48 W. Chen, J. Yang, *J. Coord. Chem.* 71 (2018) 1-19.

49 H.A. Dondas, S. Belveren, S. Poyraz, R. Grigg, C. Kilner, M. Ferrándiz-Saperas, E. Selva, J.M. Sansano, *Tetrahedron* 74 (2018) 6.

50 H.A. Döndaş, M.G. Retamosa, J.M. Sansano, *Organometallics* 38 (2019) 1828.

51 V.M. Chernyshev, A.V. Astakhov, I.E. Chikunov, R.V. Tyurin, D.B. Eremin, G.S. Ranny, V.N. Khrustalev, V.P. Ananikov, *ACS Catal*. 9 (2019) 2984.

52 O. Chidi, I.V. Adebayo, *Mod. Chem. Appl.* 6 (2018) 251.

53 U. Anand, C. Jash, S. Mukherjee, *J. Colloid Interface Sci.* 364 (2011) 400.

54 a) W.C. Griffin, *J. Soc. Cosmet. Chem*. 1 (1949) 311; b) W.C. Griffin, *J. Soc. Cosmet. Chem.* 5 (1954) 249.

55 S.K. Hait, S.P. Moulik, *J. Surfact. Deterg*. 4 (2001) 303.

56 B. Lü, C. Fu, S. Ma, *Tetrahedron Lett.* 9 (2010) 1284.

57 L. Ackermann, A. Althammer, *Org. Lett*. 8 (2006) 3457.

58 P. Gribanov, Y. Golenko, M. Topchiy, A. Asachenko, M. Nechaev, *Eur. J. Org. Chem*. (2018) 120.

59 J. Hamdi, A. Blanco, B. Diehl, J. Wiley, M. Trudell, *Org. Lett*. 21 (2019) 3471.

60 K. Pill-Seong, K. Sung-Bo, J. Myoun, J. Park, *Bull. Korean Chem. Soc*. 30 (2009) 2697.

61 F. Khosravi, M. Gholinejad, D. Lledó, G. Grindlay, C. Nájera, J.M. Sansano, *J. Organomet. Chem.* 901 (2019) 120941.

62 Y. Luan, T. Zhang, W. Yao, K. Lu, L. Kong, Y. Lin, M. Ye, *J. Am. Chem. Soc*. 139 (2017) 1786.

63 L. Wang, Y. Wei, Y. Zhao, X. Duan, *J. Org. Chem.* 84 (2019) 5176.

64 M. Kuroboshi, Y. Waki, H. Tanaka, *J. Org. Chem.* 10 (2003) 3938.

65 Z. Peng, G. Hu, H. Qiao, P. Xu, Y. Gao, Y. Zhao, *J. Org. Chem.* 79 (2014) 2733.

66 Y. Monguchi, T. Hattori, Y. Miyamoto, T. Yanase, Y. Sawama, H. Sajiki, *Adv. Synth. Catal*. 354 (2012) 2561.

67 N. Liu, C. Liu, Z. Jin, *Green Chem.* 14 (2012) 592.

68 P. Li, L. Wang, L. Zhang, G.W. Wang, *Adv. Synth. Catal.* 354 (2012) 1307.

69 P. Mao, L. Yang, Y. Xiao, J. Yuan, X. Liu, M. Song, *J. Organomet. Chem*. 705 (2012) 39.

70 N.E. Costa, A.L. Pelotte, J.M. Simard, C.A. Syvinski, A.M. Deveau, *J. Chem. Educ*. 89 (2012) 1064.

71 Y. Li, K. Wang, Y. Ping, Y. Wang, W. Kong, *Org. Lett.* 20 (2018) 921.

HIGHLIGHTS

Resistant micellar palladium nanoparticles

Sustainable palladium-catalysed Suzuki-Miyaura coupling

Highly recoverable micellar palladium nanoparticles

Bromo/iodoarenes react with boronic acids using micellar palladium nanoparticles

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: