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ARTICLE

Heterogeneous C–H Alkenylations in Continuous-Flow: Oxidative Palladium-Catalysis in a Biomass-Derived Reaction Medium

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Francesco Ferlin,[a] Stefano Santoro,[a] Lutz Ackermann*[b] and Luigi Vaccaro*[a]

Herein we report the unprecedented Fujiwara-Moritani reaction catalysed by commercially available heterogeneous palladium catalyst Pd/C. The reaction works efficiently in GVL, a biomass derived solvent, in the coupling between variously substituted acetanilides and electron-poor alkenes, with complete selectivity towards the *ortho*-substitution. Moreover, the catalyst can be easily recycled and reused for consecutive reaction runs. We also developed a continuous-flow procedure, through an easily accessible tailor-made reactor, which allows the production of the C–H alkenylated products in grams per hour scale.

Introduction

In recent years, major efforts have been directed towards the development of methodologies that allow the direct functionalisation of generally inert C–H bonds.[1] The vast majority of the protocols reported to date make use of soluble transition metals complexes as catalysts, thus operating in homogeneous reaction conditions. The main focus of the research in this field has been the definition of catalytic systems that would enable the C–H functionalisation to occur under mild reaction conditions and with good selectivity.[2] At the same time, there has been an increasing interest in the design of more sustainable protocols for C–H functionalisations, following the general need of realising chemical transformations with the least possible formation of waste and energy consumption.[3] In this respect, one approach is the use of insoluble catalysts that operate in a heterogeneous fashion.[4] This strategy ideally allows for an easy recovery and reuse of the catalyst, with consequent reduction in waste generation and costs. Moreover, the use of heterogeneous catalysts can result in a reduced metal contamination of the desired products, which is highly desirable for the practitioner in applied areas. A second, less explored approach consists in performing the desired reaction in an environmentally benign medium.[5] It is well known in fact that the vast majority of the waste generated in chemical processes derives from the use of solvents,[6] that almost universally are produced from fossil resources. The use of bio-based solvents, i.e. chemicals that can be easily obtained from renewable biomasses with very low carbon footprint, as alternative reaction media is rapidly gaining importance in organic chemistry.[7] Among these, γ-valerolactone (GVL), a derivative of lignocellulosic biomass, has demonstrated remarkable potential as a substitute for widely used dipolar aprotic solvents, such as DMF, DMAc, or NMP.[8] In a few cases, the use of GVL in place of common solvents resulted in additional desirable effects, such as reduced metal-leaching from heterogeneous palladium catalysts and improved catalyst recyclability.[8e-f]

Very recently, we reported on the use of heterogeneous palladium catalysts, simple and commercially available Pd/C and Pd/Al_2O_3, to promote C–H functionalisation reactions, such as the Catellani reaction[8c] and the C–H arylation of 1,2,3-triazoles.[8d] In both cases the reactions were conducted in GVL as reaction medium, the catalyst could be recovered and reused without loss of efficacy, and the products were isolated with very limited palladium content.

The Fujiwara-Moritani (FM) reaction is the palladium-catalysed direct coupling of arenes with alkenes.[9] The main advantage over the classical Mizoroki-Heck reaction is that the FM reaction does not require a prefunctionalisation of the aromatic coupling partner, since the aryl-palladium intermediate is generated through a C–H activation step. The FM reaction thus offers a straightforward entry to aryl alkenes, with wide potential application in organic synthesis. Typically, FM reactions are catalysed by a palladium(II) salt and are accelerated by the presence of Brønsted acids. It is quite common indeed to use the acid as the sole reaction medium, with possible consequences in terms of functional groups tolerance. Concerning the oxidant, the most used ones are $Cu(OAc)_2$ and 1,4-benzoquinone (BQ), with relatively few examples using air or molecular oxygen.[10]

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[a] Laboratory of Green Synthetic Organic Chemistry, Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy. E-mail: luigi.vaccaro@unipg.it.
[b] Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Tammannstrasse 2, 37077 Göttingen, Germany. E-mail: Lutz.Ackermann@chemie.uni-goettingen.de.

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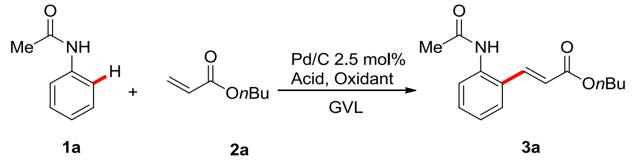
Our long-standing research interest in the development of sustainable chemical processes[11] and our recent findings concerning the use of heterogeneous catalysts in GVL for palladium-catalysed reactions[8c-g] prompted us to investigate the possibility to develop a sustainable Fujiwara-Moritani reaction.

Results and discussion

We began our study by reacting acetanilide (**1a**) with butyl acrylate (**2a**) using 2.5 mol% of Pd/C (10% wt) as catalyst in GVL (Table 1). We found that the reaction occurs smoothly with 16 equivalents of acetic acid and 2 equivalents of either $Cu(OAc)_2$ or BQ as oxidant at 150 °C, affording exclusively the desired *ortho*-functionalised product (**3a**) in 85-90% in 24 hours (Table 1, entries 1 and 2). Changing the additive to *p*-toluenesulfonic acid (TsOH) allowed to reduce the amount from 16 to 1 equivalent. Also, while the two tested oxidants gave similar results when used in combination with AcOH, the reaction with TsOH is more efficient with BQ than with AcOH (Table 1, entries 3 and 4). Indeed, TsOH in combination with BQ also allowed to reduce the reaction temperature to 85 °C. Finally, we also tested the reaction using a polymer-bound *p*-toluenesulfonic acid (PS-TsOH), since this would allow for an easier recover and reuse of the additive together with the catalyst (Table 1, entry 5). We were delighted to find that using just 1 equivalent of this supported acid, with 2 equivalents of BQ at 85 °C led to obtain product **3a** in a striking 95% yield.

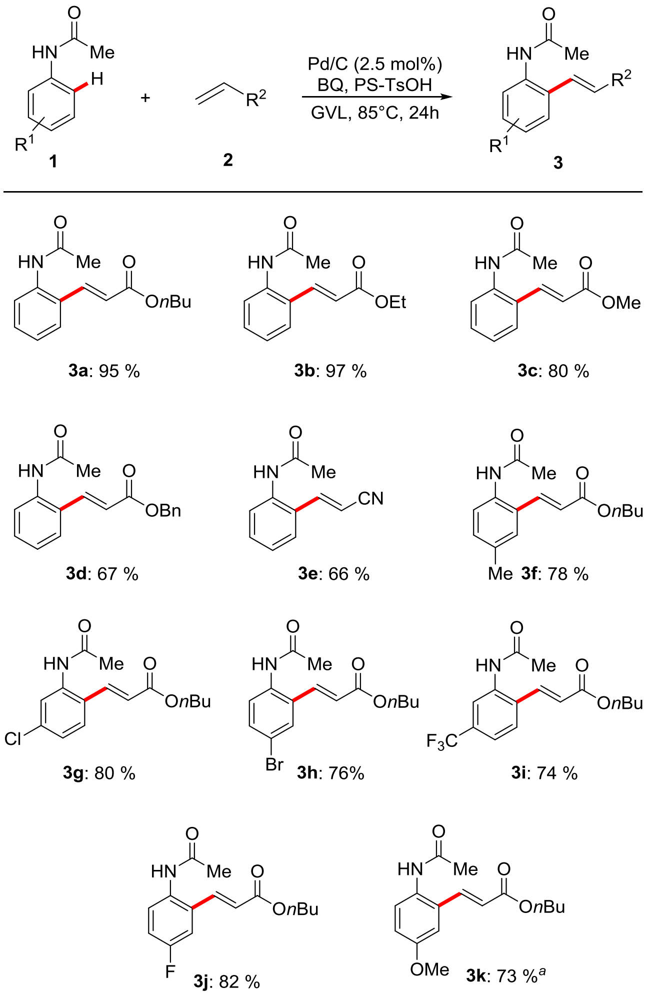
Table 1. Optimization of reaction conditions for the Fujiwara-Moritani reaction in GVL.[a]



Entry	Acid	Oxidant	T (°C)	Yield
1	AcOH (16 eq)	$Cu(OAc)_2$ (2 eq)	150	90%
2	AcOH (16 eq)	BQ (2 eq)	150	85%
3	TsOH (1 eq)	$Cu(OAc)_2$ (2 eq)	150	65%
4	TsOH (1 eq)	BQ (2 eq)	85	87%
5	PS-TsOH (1 eq)	BQ (2 eq)	85	95%

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.55 mmol), Pd/C (2.5 mol%), GVL (1 mL), 24h.

These latter reaction conditions were subsequently used to explore the scope of the Fujiwara-Moritani reaction, using a variety of substituted acetanilides and alkenes (Scheme 1). Gratifyingly, the mono-alkenylation occurred selectively in the *ortho*-position of acetanilide (**1a**) in the reaction with various electron-poor alkenes, such as butyl acrylate, ethyl acrylate, methyl acrylate, benzyl acrylate and acrylonitrile. Substituted acetanilides, functionalized with either electron-withdrawing or -donating groups, were also competent substrates, generally affording the product of mono-alkenylation in the *ortho*-position relative to the acetamido-group, confirming the excellent ability of this functionality in directing C–H activation processes. Importantly, the presence of halide substituents on the aromatic substrate is well tolerated, which paves the way to further orthogonal functionalisations through classical cross-coupling processes. In all the cases, the expected products were obtained in good to excellent yields, without noticeable formation of any side products.



Scheme 1. Scope of the Pd/C-catalysed Fujiwara-Moritani reaction in GVL. Reaction conditions: **1** (0.5 mmol), **2** (0.55 mmol), Pd/C (2.5 mol%), PS-TsOH (0.5 mmol), BQ (1 mmol), GVL (1 mL), 85 °C, 24h. [a] Reaction conducted with 5 mol% of Pd/C and 1 mmol of **2** for 48h.

Crucial to our design of a sustainable process is the possibility to efficiently recover and reuse the catalytic system, in this case comprising the palladium catalyst and the polymer-supported acid. We found that the catalyst/acid mixture can be easily and efficiently reused for at least five consecutive runs of the reaction between **1a** and **2a**, without noticeable loss of activity until the fourth run, and a limited reduction of product yield in the fifth run (Table 2). Moreover, the amount of metal released into the reaction medium was measured after each run by ICP-OES analysis, which revealed that metal-leaching from the supported catalyst is consistently very limited (ca. 4 ppm, see Table 2). At this stage we also performed a hot-filtration test and a Hg-poisoning test, in order to get insights into the nature of the catalytically active species. The results of these tests suggest a possible heterogeneous catalysis (see SI for details), although a “release and catch” mechanism[12] is probably more likely, given the reaction conditions and the well-known mechanism of the FM reaction. To the best of our knowledge, this is the first example of a FM reaction promoted by a simple and commercially available operationally heterogeneous catalyst that can be easily and efficiently recycled.[13]

Table 2. Catalyst recycling for the reaction between **1a** and **2a** in batch.[a]

	Run 1	Run 2	Run 3	Run 4	Run 5
Yield	95%	95%	94%	93%	87%
Pd leaching (ppm)	4.0	3.7	3.8	4.1	4.2

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.55 mmol), Pd/C (2.5 mol%), GVL (1 mL), 85 °C, 24h.

The stability of the heterogeneous catalyst, i.e. its ability to reliably promote the reaction for consecutive reaction runs, led us to explore the possibility of scaling-up the process in continuous flow.[14] This approach is particularly suited for heterogeneous catalysis, with beneficial consequences such as the possibility to reduce the amount of solvent and the increased mechanical stability of the catalyst.[15] Thus, after preparing a tailor-made reactor (see SI for details) we pumped into it a GVL solution of the reactants (**1a** and **2a**, 430 mmol scale), BQ and TsOH at a 0.5 mL·min^{-1} flow rate. After 29 hours 109 grams of product **3a** were obtained in 97% yield, demonstrating the suitability of this approach for medium-scale continuous productions (Figure 1). Measuring the amount of palladium released into the GVL solution by ICP-OES analysis revealed limited metal leaching from the heterogeneous support (ca. 4 ppm, see Figure 2), comparable to that observed in batch conditions. In addition, GVL proved not only to be a safer and greener polar aprotic solvent but also a more chemically efficient alternative to classic and toxic polar aprotic solvents as DMF and NMP. In fact, palladium leaching was significantly lower in GVL than in DMF and NMP (ca. 4 ppm vs 80 and 31 ppm, respectively) suggesting that also the durability of the catalyst is higher in GVL than in these solvents.

We also tested the flow procedure for the reaction with different acrylates and substituted anilides (see Figure 1), obtaining in all cases excellent results in terms of product yields (87-99%) and selectivities.

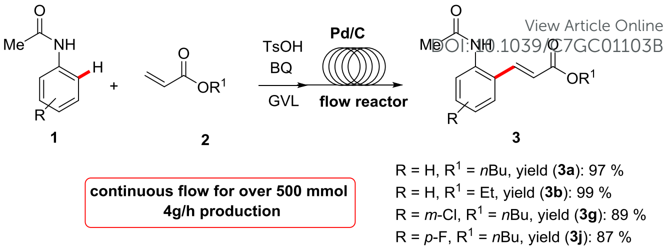


Figure 1. Continuous-flow Fujiwara-Moritani reaction.

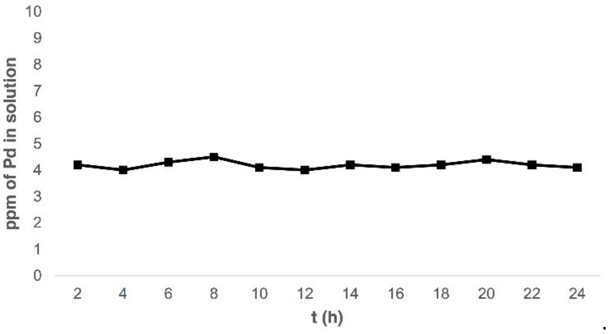


Figure 2. Palladium leaching into solution in the continuous-flow Fujiwara-Moritani reaction between **1a** and **2a**.

Conclusions

In conclusion, we have shown that the Fujiwara-Moritani C–H alkenylation reaction of acetanilides can be efficiently catalysed by simple and commercially available Pd/C in biomass-derived GVL as reaction medium. The *ortho*-functionalized products are obtained in good to excellent yields, and the catalyst can be easily recovered and reused for consecutive reaction runs. Moreover, the process could be performed in continuous flow conditions using a tailor-made packed reactor. Performing the reaction in flow has additional advantages in terms of shorter reaction times and improved recoverability and durability of the catalyst.

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