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ARTICLE TYPE

γ -Valerolactone as an alternative biomass-derived medium for the Sonogashira reaction.

Giacomo Strappaveccia,^a Lorenzo Luciani,^a Elena Bartollini,^a Assunta Marrocchi,^a Ferdinando Pizzo,^a Luigi Vaccaro^{a*}

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γ -Valerolactone (GVL) can be used as an efficient and practical alternative to the banned and commonly used dipolar aprotic solvents. In this contribution GVL has been used as a non-toxic, biodegradable, biomass-derived medium, for the definition of a simple and general protocol for the Sonogashira cross-coupling reaction. The chemical efficiency of GVL as medium is excellent and the best results have been obtained using DABCO as base allowing to isolate products **3a-q** in 60-96% yields. These results represent an example that proves that biomass-derived safer solvents can be used efficiently in common transformations reaching higher greenness/sustainability as well as high chemical efficiency.

Introduction

Although crude oil still remains a major feedstock for the chemical industry, sustainability issues are directing attention towards the definition of alternative materials deriving from renewable biomass¹ resources to access fuels and new building blocks for the production of chemicals/materials. Indeed, the replacement on a large scale of fossil-based fuel/chemicals for bio-based compounds is a fundamental step to consolidate the green chemistry principles in the frame of a modern and competitive chemical production.

Notably, biomass, being the only renewable source of carbon,²⁻⁵ is estimated to generate between 25-30% of the chemical commodities by 2030.³⁻⁵ In this context, a relevant research area explored in recent years deals with the development of tools which enable crude biomass deconstruction into valuable multifunctional simpler compounds (platform chemicals) that can be consequently converted into value-added chemicals, fuels and materials.^{6,7}

Among the building blocks, an ever increasing attention is currently directed to γ -valerolactone (GVL), owing to its peculiar chemical-physical properties which enable its use as a fuel additive, solvent, as well as an ideal precursor for the production of alkanes, alkenes, and valuable chemicals.⁸ GVL is conventionally produced from lignocellulosic biomass-derived levulinic acid^{9,10} and its esters via (catalytic) hydrogenation. The use of GVL as solvent is particularly interesting since in many well-established chemical processes large amounts of organic volatile compounds are used as reaction media and for separation, which constitute, in addition, the largest percentage of all the associated waste, thereby posing serious health/environmental concerns.^{11,12}

In this regard, the identification of green bio-based solvents deriving from renewable resources is therefore crucial.¹³ Among

all the type of solvents the dipolar aprotic media feature the major issues. This class of solvents is very useful to chemists, but nowadays they are under strict environment, health and safety regulations due to their toxicity and environmental impact.¹⁴ In this context GVL may have an key role as a sustainable substituent for this class of solvent. GVL has many excellent properties^{15,16} that allow it to be an ideal choice of sustainable alternative to conventional polar aprotic solvents. For instance, its polarity¹⁵ is very similar to that for the most common; indeed, the dielectric constant of GVL at 25 °C is 36.47 whereas those measured at the same temperature for CH₃CN, DMF, NMP and DMA are 37.5, 36.7, 32.0 and 37.8, respectively. Moreover, it features low melting (-31°C) and high boiling (207°C) points, and a flash point (96°C) which is generally higher than those for conventional dipolar aprotic solvents including CH₃CN (2°C), DMF (58 °C), NMP (61°C), and DMA (63°C). In addition, GVL vapor pressure is 0.65 kPa at 25 °C, and, notably, it increases only to 3.5 kPa at 80 °C. Finally, it is quite stable under neutral conditions, and, particularly, it does not form measurable amounts of peroxides in a glass flask under air within few weeks, which makes it a safe material for use on a large scale.

To prove that GVL may be a valid replacement for common polar aprotic solvents we developed an efficient protocol for the palladium on activated charcoal (Pd/C) catalyzed Sonogashira cross-coupling reaction (Scheme 1), which is often performed in e.g. dimethylformamide (DMF).¹⁷

Although a number of reports on the use of GVL to replace conventional polar aprotic solvents in chemical processes exist,¹⁸ to the best of our knowledge this is the first case for Sonogashira coupling.

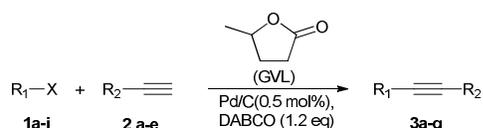
Our findings demonstrated that GVL is a promising polar medium to synthesize a number of acetylene-containing systems in high yields and in a more sustainable way. Further, we demonstrated that GVL enable a far better control of palladium

leaching into the final products compared to a number of more conventional polar solvents, thereby enhancing the characteristics of the recyclability of the catalyst system as well as limiting the contamination of the products themselves with traces of heavy metals.

We believe that this new utilization of GVL would importantly allow it to broaden its scope to move forward in catalyzing the switching process from an unsustainable oil-based economy to a more sustainable biomass-based one.

10 Results and discussion

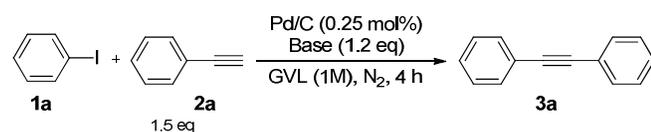
To verify the applicability of GLV as reaction medium for the Sonogashira cross-coupling reaction, we employed first iodobenzene (**1a**) and phenylacetylene (**2a**) as reference substrates by testing several protocol conditions. Next, we decided to broaden the substrate scope and apply the selected conditions to a sterically hampered phenylacetylene and alkyl-substituted alkynes (Scheme 1).



20 **Scheme 1** Protocol for the Sonogashira cross-coupling reaction performed in GVL.

Notably, we focused on the cheap, ligand-free Pd/C catalytic system,¹⁹ avoiding any co-catalyst, to render the protocol as general as possible.

Table 1. Screening of the bases in the Sonogashira reaction between **1a** and **2a**.



Entry	Base	T (°C)	Conversion (%) ^b
1	Triethylamine	60	25
2	Triethylamine	100	59
3	Piperidine	60	42
4	Piperidine	100	82
5	Pyrrolidine	60	28
6	Pyrrolidine	100	40
7	Diisopropylamine	60	36
8	Diisopropylamine	100	50

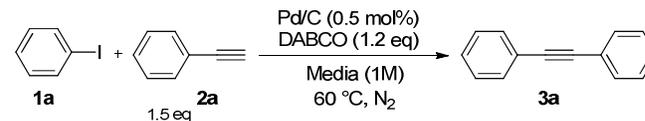
9	K ₂ CO ₃	100	13
10	KOH	100	23
11	Tetrabutylammonium acetate	60	79
12	Tetrabutylammonium acetate	100	93
13	DABCO	60	91
14	DABCO	100	92
15 ^a	DABCO	60	>99
16 ^b	DABCO	60	95
17 ^c	DABCO	60	94

30 ^a Performed with 0.5 mol% of Pd/C. ^b Performed with 1 equiv of DABCO. ^c Performed with 1.2 equiv of phenylacetylene.

Thus, we investigated first the Sonogashira GVL protocol optimization using iodobenzene (**1a**) and phenylacetylene (**2a**) as reference substrates, by employing several type of amines, commonly used for more conventional Sonogashira's protocols, e.g. triethylamine, piperidine, pyrrolidine and diisopropylamine, at different temperatures ranging from 60° to 100 °C (Table 1, entries 1-8).

40 We obtained unsatisfactory results, the best conversion being 82% at 100 °C in the presence of piperidine (Table 1, entry 4).

Table 2. Screening of reaction media and data for palladium leaching in the Sonogashira cross-coupling between **1a** and **2a**.



Entry	Solvent	Time (min)	Conversion (%)	Yield (%)	Pd leaching (ppm)
1	DMF	5	100	70	617±5
2	NMP	5	100	73	144±2
3	DMSO	10	100	69	384±4
4	CH ₃ CN	30	100	72	424±4
5	GVL	240	100	70	19±0.2
6	H ₂ O	240	76	n.p.	n.p.
7	Toluene	240	90	n.p.	n.p.
8	THF	240	70	n.p.	n.p.

45 Using inorganic bases such as potassium carbonate and potassium

hydroxide (Table 1, entries 9 and 10) we had very low conversions even at temperatures as high as 100 °C, likely owing to their low solubility in the reaction media. Better results were obtained by employing tetrabutylammonium acetate, with a conversion of 93% at 100 °C (Table 1, entry 12). However, the best-performing base was 1,4-diazabicyclo[2.2.2]octane (DABCO), with which we achieved a conversion of 91% at 60 °C (Table 1, entry 13). The higher reactivity of DABCO compared to other bases can be ascribed to its double double role as a base and as a ligand. It has been already reported that its use in the Sonogashira reaction,²⁰ led to an enhanced catalytic efficiency if compared to other bases. Higher reaction temperatures (100 °C) didn't influence the reactivity of the system (Table 1, entry 14), whereas by increasing the catalyst loading from 0.25 mol% to 0.5 mol% (Table 1, entry 15) we reached the complete conversion of **1a** into product **3a**. Moreover, we tried to further optimize the reaction conditions by lowering the amount of the base used from 1.2 to 1 equivalent, or reducing the equivalents of phenylacetylene substrate (Table 1, entries 16 and 17, respectively), but in all cases the reactions didn't reach completeness.

Next, we analyzed the behaviour of our system in different media (Table 2 and Figure 1). We carried out the reaction in common dipolar aprotic solvents such as DMF, NMP, DMSO and CH₃CN, and we found that in these solvents the reactivity of the substrates was higher than that in GVL. More in details, the reaction went to completion after only 5 minutes when DMF and NMP were employed (Table 2, entries 1-2), whereas it took 10 minutes to occur by using DMSO (Table 2, entry 3) and half an hour in CH₃CN (Table 2, entry 4). On the other hand, the reaction in GVL went to completion after 4 hours (Table 2, entry 5). The dielectric constant for all the employed media is quite similar, therefore a polarity effect on the reaction, is likely rather limited. This behavior may therefore be explained with a higher leaching of palladium species in the reaction mixture when using conventional polar solvents, due to the higher complexing ability of these latter towards palladium,²¹ which may account for a different catalytic activity.

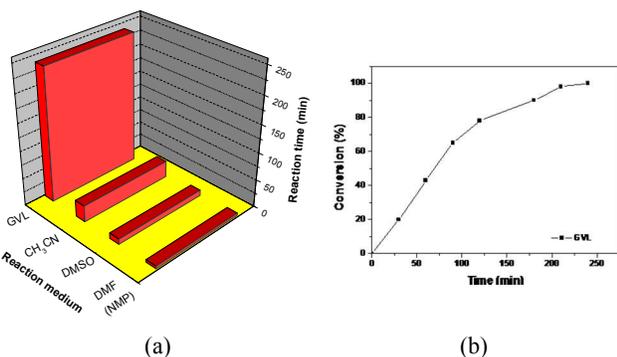


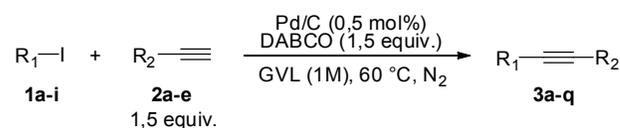
Figure 1. (a) Diagram illustrating the influence of the reaction medium on the reaction time for Sonogashira cross-coupling between **1a** and **2a** (100% conversion in **3a**); (b) Conversion vs reaction time plot for Sonogashira cross-coupling between **1a** and **2a** in GVL

amount of leached palladium into the final products. Indeed, when the reaction is performed in GVL, the metal product contamination markedly decreases. (Table 2, entries 1-4 vs 5). It is important to underline that the yields of the reaction performed in these polar aprotic solvents remained similar, ranging from 69 to 73% (see Yield column in Table 2).

Furthermore, we demonstrated that by performing the reaction in a number of not dipolar aprotic media, i.e. water, toluene or THF, which are also commonly used for the Sonogashira cross-couplings, the system showed lower reactivity (Table 3, entries 6-8). This data underlined that the use of a dipolar aprotic solvent is preferable for Sonogashira reaction, and among them GVL only can be identified as a green solvent.

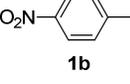
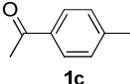
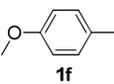
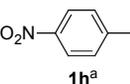
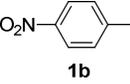
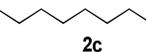
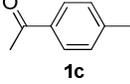
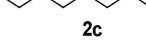
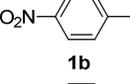
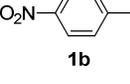
Next, we applied the optimal reaction conditions to other substrates (Table 3). Under these conditions we obtained good reactivity for a wide range of aryl iodide substrates, including both activated substrates, such as 4-nitro-iodobenzene (**1b**), 4'-iodoacetophenone (**1c**) and 4-iodobenzaldehyde (**1d**) (Table 3, entries 2-4) and deactivated substrates such as 4-iodotoluene (**1e**) or 4-iodoanisole (**1f**) (Table 3, entries 5 and 6). Moreover, 2-iodothiophene heterocycle (**1g**) reacted in good yield (Table 2, entry 7) as well as bromo-derivatives **1h-i** (Table 3, entries 8 and 9).

Table 3. Substrate scope of the Sonogashira reaction in GVL.



Entry	R ₁	R ₂	Time (h)	Product	Yield (%)
1			4	3a	70
2			2	3b	94
3			2,5	3c	95
4			2,5	3d	90
5			4,5	3e	80
6			5	3f	75
7			6	3g	65
8			12	3b	75
9			12	3d	70

This was corroborated also by the Inductive Coupled Plasma-Optical Emission Spectrometer (ICP-OES) measurements of the

10			4	3h	74
11			2	3i	91
12			2,5	3j	96
13			4,5	3k	70
14			5	3l	65
15			6	3m	60
16			12	3i	77
17 ^b			4,5	3n	94
18 ^b			4,5	3o	96
19 ^b			4,5	3p	87
20 ^b			6	3q	61

^a The bromo derivative was used. ^b 2 equiv of DABCO were used.

We also successfully extended the protocol to a sterically hampered phenylacetylene, the 1-ethynyl-2-(trifluoromethyl)benzene (**2b**), obtaining results similar to those for phenylacetylene **2a** (Table 3, entries 10-16). Finally, to further broaden the scope of the GVL-based Sonogashira reaction, we included as substrates two alkyl-substituted alkynes, i.e. oct-1-yne (**2c**) and hex-1-yne (**2d**) (Table 3, entries 17-19), and ethynyltrimethylsilane (**2e**) (Table 3, entry 20). In all cases, a few percent amount of homo-coupling products was detected (<4%), although conversion of (hetero)aryl iodides was complete. Good to high reaction yields were achieved.

Conclusions

In conclusion, we have reported the use of GVL as a non-toxic, biodegradable, biomass-derived medium. We have demonstrated that GVL can be used as an efficient and practical alternative to the banned and commonly used dipolar aprotic solvents. In particular, our attention has been devoted to strategic carbon-carbon coupling reaction widely used in organic synthesis such as

Sonogashira reaction.

In this context, we found that the chemical efficiency of GVL as medium is excellent and the best results have been obtained using DABCO as base. The protocol has been extended to a wide range of substrates and several products **3a-q** have been isolated satisfactorily to very high yields, comparable to other known procedures using toxic media.¹⁹

This contribution is also aimed at demonstrating within chemistry community that safer solvents can be used efficiently in common transformations reaching higher greenness/sustainability as well as high chemical efficiency. The use of GVL in strategic processes may significantly reduce the environmental impact and energy cost of the chemical industry.

Further investigations are ongoing to prove that GVL is a more general and promising alternative for the critical replacement of common toxic polar media.

Experimental Section

Unless otherwise stated, all solvents and reagents were used as obtained from Sigma-Aldrich Co. without further purification. Commercial Pd/C (10% wt) was not activated prior to use, and the value of palladium loading of the catalyst was taken from its certificate of analysis available at <http://www.sigmaaldrich.com>. commercial sources without any further purification. GLC analyses were performed by using Hewlett-Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.53 mm), a FID detector and hydrogen as gas carrier. GC-EIMS analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV.

NMR spectra were recorded on a Bruker DRX-ADVANCE 200 MHz and a Bruker DRX-ADVANCE 400 MHz (1 H at 400 MHz and 13 C at 100.6 MHz) in CDCl₃, and TMS was employed as internal standard. Elemental analyses were conducted on a FISONs instrument EA 1108 CHN. Melting points are not corrected and they were measured on a Büchi 510. An Inductive Coupled Plasma-Optical Emission Spectrometer (ICP-OES 710 Agilent Technology) was used to determine the amount of leached palladium into the reaction products.

Compounds **3a**¹, **3b**¹, **3c**¹, **3d**², **3e**¹, **3f**¹, **3g**³, **3h**⁴, **3i**⁴, **3j**⁴, **3k**⁵, **3l**⁴, **3m**⁵, **3n**⁶, **3o**⁶, **3p**⁶, **3q**⁷ are known compounds.

Experimental procedures for compounds **3a-q**, characterization data and copies of the ¹H and ¹³C-NMR are reported in the Electronic Supplementary Information (ESI).

Representative experimental procedure for the Sonogashira protocol. Synthesis of compound **3a**.

In a screw capped vial equipped with a magnetic stirrer Pd/C 10% wt. (5.3 mg, 0.5 mmol%), GVL (1 mL), DABCO (139 mg, 1.2 mmol, 99% purity), iodobenzene (**1a**) (208 mg, 0.114 mL, 1 mmol, 98% purity), and ethynylbenzene (**2a**) (156 mg, 0.168 mL, 1.5 mmol, 98% purity) were consecutively added and the resulting mixture was purged with nitrogen and left under stirring at 60 °C. After reaction completion, petroleum ether was added and the reaction mixture was filtered over a small pad of celite, washed with neutral water and, subsequently, with acidic water

(1 M HCl). The organic layer was dried over sodium sulphate and the solvent was removed under vacuum. The crude oil was purified by column chromatography on silica gel (petroleum ether) to obtain 1,2-diphenylethyne (**3a**) as a white solid (124 mg, 70% yield).

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^a Dr. G. Strappaveccia, Dr. L. Luciani, Dr. E. Bartollini, Dr. A. Marrocchi, Prof. F. Pizzo, Prof. L. Vaccaro, Laboratory of Green Synthetic Organic Chemistry, CEMIN – Dipartimento di Chimica, Biologia e Biotecnologie, Università di Perugia Via Elce di Sotto 8, 06123 Perugia, Italia. Fax: +39 075 5855560; Tel: +39 075 5855541; E-mail: luigi.vaccaro@unipg.it

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