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Synthesis of 2-Alkylaryl and Furanyl Acetates by Palladium Catalysed Carbonylation of Alcohols

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Abstract: The one-pot alkoxycarbonylation of halo-free alkylaryl and furanyl alcohols represents a sustainable alternative for the synthesis of alkylaryl and furanyl acetates. In this paper, the reaction between benzyl alcohol, chosen as a model substrate, CH_3OH and CO was tested in the presence of a homogeneous palladium catalyst, an activator (isopropenyl acetate (IPAc) or dimethyl carbonate (DMC)) and a base (Cs_2CO_3). The influence of various reaction parameters such as the CO pressure, ligand and palladium precursor employed, mmol% catalyst load, temperature and time were investigated. The results demonstrate that decreasing the CO pressure from 50 bar to 5 bar at 130 °C for 18 h increases yields in benzyl acetate from 36% to over 98%. Further experiments were performed in the presence of piperonyl and furfuryl alcohol, interesting substrates employed for the synthesis of various fine chemicals. Moreover, furfuryl alcohol is a lignocellulosic-derived building block employed for the synthesis of functionalized furans such as 2-alkylfurfuryl acetates. Both the alcohols were successfully transformed in the corresponding acetate (yields above 96%) in rather mild reaction conditions (5–0.01 mol% catalyst, 5–2 bar CO pressure, 130 °C, 4–18h), demonstrating that the alkoxycarbonylation of alcohols represents a promising sustainable alternative to more impactful industrial practices adopted to date for the synthesis of alkylaryl and furfuryl acetates.

Keywords: alkoxycarbonylation; one-pot synthesis; alkylaryl acetate; furanyl acetate; benzyl alcohol; piperonyl alcohol; furfuryl alcohol; homogeneous palladium catalyst; DPPF

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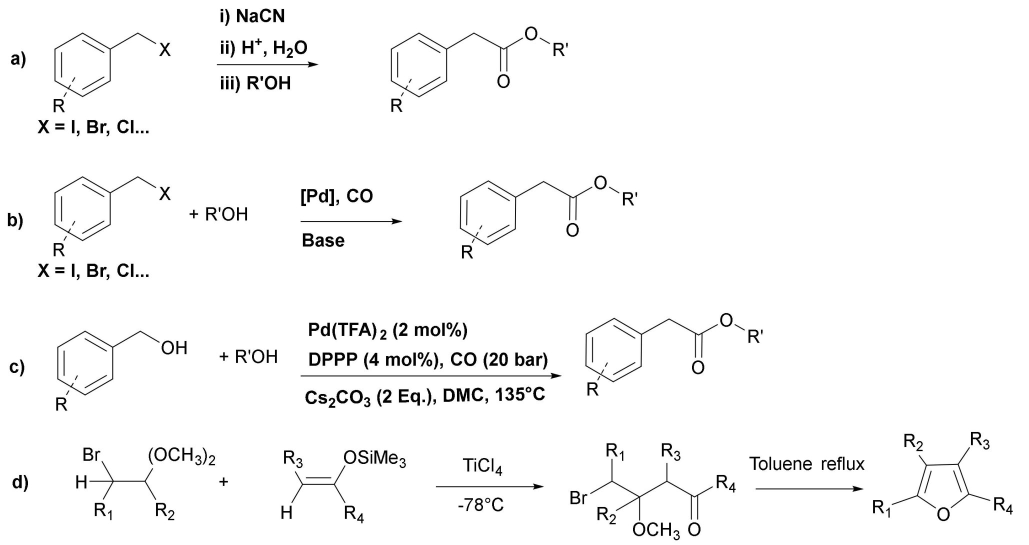
1. Introduction

Within the boundaries of green chemistry and green transition, the need for new environmentally sustainable products and processes for fine chemicals production is rapidly increasing [1–3]. In this context, alkylbenzyl and furanyl acetates and their derivatives play a crucial role for fine chemical production [4–7]. Several synthetic approaches to alkylaryl and furanyl acetates have previously been reported in the literature [8–13]. In particular, benzyl acetates are generally prepared via a multi-step synthetic strategy starting from benzyl halides and making use of harmful and toxic reagents such as sodium cyanide and strong acids (Scheme 1a–c) [14–16].

Furanyl compounds are commonly prepared by Lewis-acid-mediated condensation reactions of silyl enol ethers with aldehydes and acetals [17–20]. For example, a multi-step strategy has been reported by Mukaiyama and co-workers, foreseeing the reaction between silyl enol ethers and α-bromoacetals in the presence of $TiCl_4$ to give β-alkoxy-γ-bromoketones, which are further converted into substituted furans on refluxing in toluene (Scheme 1d) [21]. Other interesting examples for the synthesis of furans have been reported by reaction of 1,3-bis-silyl enol ethers 1,3-dicarbonyl dianions, 1,3-bis-silyl enol ethers or 1-methoxy-3-trimethylsilyloxy-1,3-butadiene and aldehydes or acetals [22–28]. These methodologies nevertheless often require complicated, multistep reaction schemes leading to an overall low product yield, high costs and very low atom efficiency.



Scheme 1. Conventional procedures for the synthesis of alkyl aryl acetates (**a**–**c**), and (**d**) furanyl compounds.

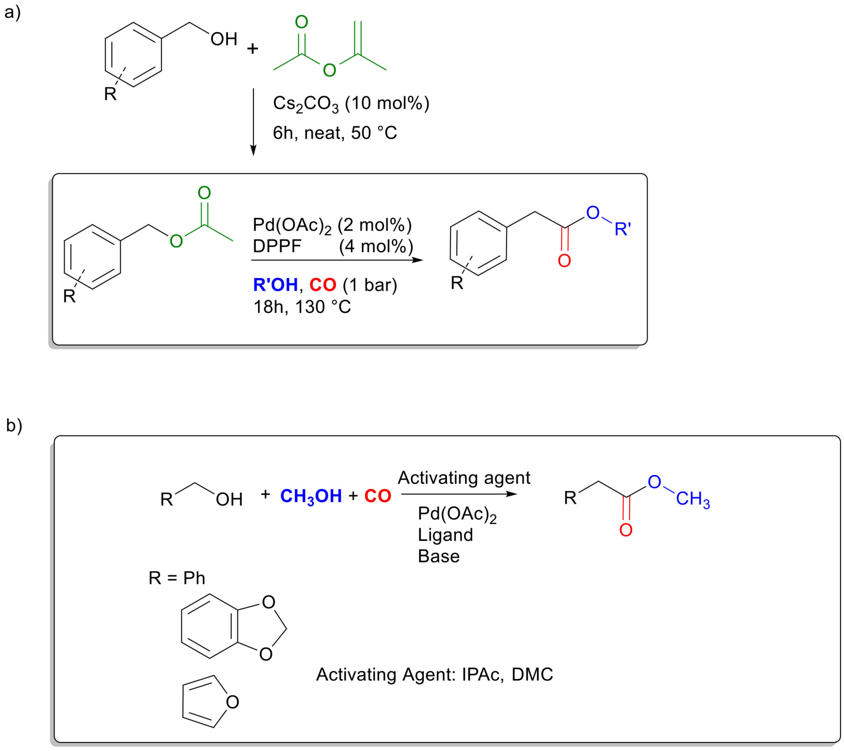
Today, furfuryl alcohol emerges as an ideal and sustainable biobased starting product for the synthesis of functionalized furans such as 2-alkylfurfuryl acetates reported in this study. Furfuryl alcohol is obtained by the hydrogenation of furfural, in turn derived from lignocellulosic biomass [29–31].

From a sustainability point of view, the use of biomass-derived building blocks constitutes a great advantage of substituting non-renewable fossil-based ones. Biomasses are carbonaceous sources and are often obtained as by-products from the agroindustry, and in many cases, end up becoming a waste [32–35]. It is estimated that around 200 billion tons of biomass is produced annually and only 3% is exploited [35]. For this reason, an increasing number of studies are in progress to valorise bio-waste, which is an extraordinary reservoir of carbon and represents a valid alternative to traditional fossil-based sources. To date, biomass cannot completely substitute fossil-based products, but it can nevertheless contribute to the transition towards an eco-sustainable future [32–35].

The main sources of biomass currently exploited to produce furfuryl alcohol are lignocellulosic and hemicellulose-derived monosaccharides derived also from vegetable waste. They include, among others, sugar cane bagasse, rice shells, corncob, and sawdust [32–34].

Considering the achievements recently reported on the carbonylation of benzyl alcohols for the synthesis benzyl acetates (Scheme 2a) [8], and given our interest in the development of sustainable products and processes [36–38] and in palladium-catalysed carbonylation reactions [39–43], in this work, we deemed it interesting to verify whether the two-step strategy developed by us for the synthesis of alkylaryl acetates could be further implemented into a one-pot strategy starting from alkylaryl and furanyl alcohols (Scheme 2b). Benzyl, piperonyl and furfuryl alcohol have been tested, the first as a standard substrate for reaction condition optimization, and the latter two as interesting examples of building blocks for fine chemical synthesis.

A one-pot strategy for the synthesis of 2-alkylbenzyl acetates and bio-based 2-alkylfurfuryl acetates starting from cheap, commercially available alcohols would represent a promising sustainable alternative to industrial practices adopted to date.



Scheme 2. (**a**) Two-step synthesis to produce 2-alkyaryl acetates [10]; (**b**) one-pot strategy, target reaction of this work.

2. Results

It is widely known that alkylaryl acetates may be synthesized by Palladium cata-lysed alkoxycarbonylation starting from benzyl halides (Scheme 1a,b) [14–16], while benzyl alcohols are seldom employed as substrates because the oxidative addition of a C(sp3)–OH group to Pd(0) species is difficult (Scheme 1c) [8,16,44,45]. Therefore, it is generally accepted that alcohols must be activated, for example, by reaction with mineral acids, to promote the oxidative addition to palladium [8]. The possibility to use alcohols as an alternative to halogenated products constitutes a great advantage both for the environment and for laborers [46].

According to the work by us [8], the binary system $Pd(OAc)_2$/DPPF (DPPF = 1,1′(Bis-diphenylphosphino)ferrocene) resulted to be the best-performing catalyst at 130 °C, P(CO) 5–20 bar for 18 h, for the alkoxy and hydroxy carbonylation of several benzyl acetates, producing the corresponding 2-alkylaryl acetates in very high yields (between 70% and 99%). In agreement with the literature [8,47], the reaction proceeds in two steps as reported in Scheme 2a.

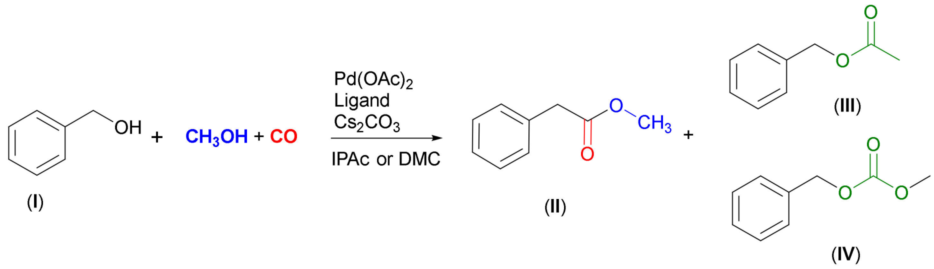
Considering that benzyl acetates are produced from the corresponding alcohol, the possibility to synthesize 2-alkylaryl and furfuryl acetates with a one-pot strategy seems extremely appealing and sustainable for reducing the process complexity, reagent and purification costs, and solvent consumption. As aforementioned, the direct carbonylation of benzyl alcohols has been scantly investigated in the past due to the harsh reaction conditions that are generally required, hazardous and corrosive reagents employed, and low selectivity to the desired products [48,49]. Thus, the development of a clean, safe, and sustainable methodology represents an attractive task.

To the best of our knowledge, there is only one example in the literature of direct alkoxycarbonylation of benzyl alcohols to alkylaryl acetate in the presence of $Pd(TAF)_2$, 1,3-bis(diphenylphosphino)propane (DPPP) and dimethyl carbonate (DMC) as green solvent and in situ activator [49]. Taking into consideration the work of Li [50] and recent results reported by Sole and co-workers [8], in this paper, a one-pot strategy is reported for the synthesis of alkylaryl and furfuryl acetates in the presence of $Pd(OAc)_2$; a diphenylphosphine such as DPPF, DPPP or 1,2-bis(diphenylphosphino)ethane (DPPE); and isopropenyl acetate (IPAc) or DMC as an activating agent.

2.1. One-Pot Methoxycarbonylation of Benzyl Alcohol (I)

Experiments were carried out using benzyl alcohol as a standard substrate to compare pros and cons of the one-pot strategy with the two-step synthetic strategy reported in the literature (Scheme 2a) [8,49]. Preliminarily, an experiment was carried out without Pd, allowing assessing that the reaction does not proceed in the absence of a metal catalyst.

The one-pot methoxycarbonylation of benzyl alcohol for the synthesis of 2-phenylmethyl acetate (**II**) (Scheme 3) was tested in the presence of $Pd(OAc)_2$/DPPF as the catalytic system, IPAc and Cs_2CO_3, screening different P(CO), at 130 °C for 18 h, as reported in Table 1. All experiments were performed in triplicate.



Scheme 3. One-pot methoxycarbonylation of benzyl alcohol (**I**).

Table 1. One-pot methoxycarbonylation of benzyl alcohol (**I**).

Entry [a]	Ctz.	P_{CO} (Bar)	Conv. (%) [b]	Yield [b]
1	$Pd(OAc)_2$	50	36	15
2	$Pd(OAc)_2$	20	56	39
3	$Pd(OAc)_2$	10	80	54
4	$Pd(OAc)_2$	5	66	49
5	$Pd(CF_3COO)_2$	5	62	24
6	$Pd(DPPF)Cl_2$ acetone [c]	5	61	24
7 [d]	$Pd(OAc)_2$	5	99	98

[a] Reaction conditions: (**I**) = 1 mmol, $Pd(OAc)_2$ = 5 mol%, DPPF = 10 mol%, Cs_2CO_3 5 mol%, IPAc = 1 mL, MeOH = 1 mL, Time = 18 h, T = 130 °C. [b] Substrate conversion and product yield were calculated by GC analysis using mesitylene as an internal standard. Differences between conversions and product yield correspond to the percentage of intermediate present in the reaction mixture. [c] Dichloro bis(diphenylphosphino)ferrocene Palladium (II) acetone. No free ligand was added. [d] DMC = 1.5 mL.

IPAc, a non-toxic, cheap, and commercially available acetylating agent, was employed in preliminary experiments as an activating agent. IPAC efficiently provides the desired acetylated intermediate (benzyl acetate, **III**) without the need for any halogen salt or strong mineral acid [8,49].

When IPAc is employed as an activating agent, the reaction proceeds via the formation of intermediate (**III**), originated by reaction between (**I**), IPAC and Cs_2CO_3. Analogously, in the presence of DMC (see below), the intermediate specie formed from (**I**) is benzyl methyl carbonate (**IV**). Differences between conversions of (**I**) and yields in (**II**), are due to the presence of either (**III**) or (**IV**) in the reaction mixture according to the different activating agents used (see Table 1). Similar considerations apply for other substrates (**V**) and (**IX**) reported below.

At P(CO) 50 bar, 130 °C for 18 h in the presence of 5 mol% $Pd(OAc)_2$, 10 mol% DPPF, 5 mol% Cs_2CO_3 with respect to the mmoles of benzyl alcohol, and IPAc/MeOH in a 1/1 (*v*/*v*) mixture, the methoxycarbonylation of benzyl alcohol (Entry 1, Table 1) gave disappointing yields in (**II**) (15%) compared to 98% achieved in the literature starting from benzyl acetate [8].

In agreement with the literature, a decrease in P(CO) brought about an improvement both in the conversion and yield in (**II**) (compare Entries 1–4, Table 1), and the best results were achieved at P(CO) 10 bar, with 80% substrate conversion and yields in (II) of 54%. It is likely that CO competes with the substrate in the coordination sphere of palladium, a behaviour which is not unusual in carbonylation reactions due to the π-acidic nature of CO [10,18,47,48]. Further experiments carried out in the presence of different Palladium precursors (Entries 5 and 6, Table 1) gave no significant improvement compared to $Pd(OAc)_2$ and were therefore not investigated further.

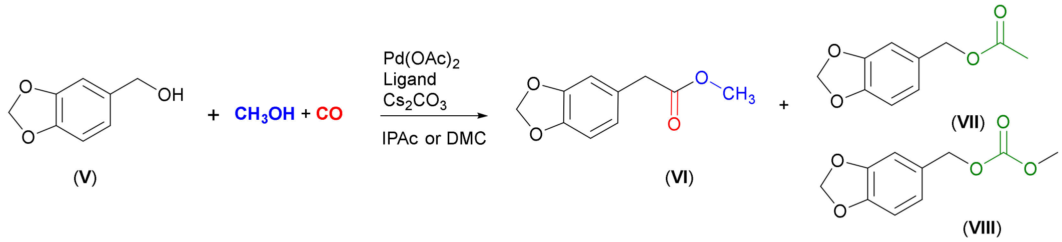
A significant improvement was observed if DMC was used as an activating agent in place of IPAc, giving almost total conversion and yield in (**II**) for 18 h at P(CO) 5 bar and 130 °C. Notably, in the presence of DMC, the intermediate specie (**III**) was totally converted to (**II**) in the reaction conditions employed (Entry 7, Table 1).

These data show the high efficiency and activity of the catalytic system as compared to data achieved with $Pd(TFA)_2$/DPPP reported by Li wherein P(CO) 20 bar was necessary to achieve over 90% yield in the desired product. Interestingly, DPPF used in combination with $Pd(TFA)_2$ was extremely inefficient [49].

These results demonstrate that the one-pot methoxycarbonylation in the presence of $Pd(OAc)_2$/DPPF and DMC is a promising tool for the direct carbonylation of alkylaryl alcohols.

2.2. *One-Pot Methoxycarbonylation of Piperonyl Alcohol (**V**)*

To widen the scope of the reaction, further experiments were carried out using piperonyl alcohol (**V**) as a substrate, in the presence of $Pd(OAc)_2$/DPPF (1/2 mol/mol), 5 mol% Cs_2CO_3 (Scheme 4) and IPAc or DMC as the activating agent. Piperonyl acetate is used as a flavour and fragrance ingredient and is an important building block for the synthesis of pharmacologically active compounds [50].



Scheme 4. Methoxycarbonylation of piperonyl alcohol (**V**).

Using optimal conditions verified with benzyl alcohol (see above), conversions in piperonyl alcohol (**V**) of 75% and yields in methyl 2-(benzo[d][1,3]dioxol-5-yl)acetate (**VI**) of 68% were achieved at P(CO) 10 bar, 130 °C for 18 h (Entry 1, Table 2). Considering that a decrease in P(CO) for the methoxycarbonylation of benzyl alcohol and benzyl acetates generally favours reaction conversions and yields in the desired product, further experiments were carried out at P(CO) 5 bar, achieving yields in (**VI**) of over 95% (Entry 2, Table 2). Furthermore, it was verified that, in the presence of DMC as the activating agent, very similar conversions and yields in (**VI**) could be achieved at a lower temperature (T 100 °C, Entry 3, Table 2).

To further improve reaction conditions, a set of experiments was carried out in the presence of DMC and lower catalyst loading (down to 0.01 mol% relative to mmol% of (**V**)), P(CO) 2 bar at 130 °C, with no significant change in conversions and yields (compare Entries 4–6, Table 2). In all cases, very low amounts of intermediate benzo[d][1,3]dioxol-5-ylmethyl methyl carbonate (**VIII**) were present at the end of the reaction (2–5%).

Table 2. One-pot methoxycarbonylation of piperonyl alcohol (**V**).

Entry [a]	A [b]	Ctz. [c]	P(CO) (bar)	T (°C)	t (h)	Conv. (%) [d]	Yield (%) [d]
							(VI)
1	DMC	5	10	130	18	75	68
2	DMC	5	5	130	18	99	95
3	DMC	5	5	100	18	95	92
4	DMC	1	2	130	18	99	96
5	DMC	0.1	2	130	18	99	94
6	DMC	0.01	2	130	18	90	90
7	IPAc	5	10	130	18	72	61
8	IPAc	5	5	130	18	99	88
9	IPAc	5	5	130	24	99	87
10	IPAc	5	2	130	18	60	36
11	IPAc	5	5	130	4	56	15
12	IPAc	5	5	100	18	28	6
13	IPAc	5	5	80	18	19	2
14	IPAc	2.5	5	130	18	85	70
15 [e]	IPAc	5	5	130	18	91	65
16 [f]	IPAc	5	5	130	18	97	40
17 [g]	IPAc	5	5	130	18	20	16

[a] Reaction conditions: (**V**) = 1 mmol; MeOH = 1 mL; Cs_2CO_3 = 5% mol, Ligand/$Pd(OAc)_2$ = 2/1, Ligand = DPPF. [b] A = activating agent, DMC = 1.5 mL, IPAc = 1.0 mL. [c] Mmol of $Pd(OAc)_2$ as refers to mmol of substrate. [d] Substrate conversion and product yield were calculated by GC analysis using mesitylene as an internal standard. Differences between conversions and product yield correspond to the percentage of intermediate present in the reaction mixture. [e] Ligand = DPPP. [f] Ligand = DPPE. [g] Ligand = PPh_3.

Further experiments were carried out in the presence of IPAc (Entries 7–17, Table 2) to study the influence of the activating agent. In reaction conditions similar to the ones adopted for (**I**), the methoxycarbonylation of (**V**) proceeded smoothly both in the presence of DMC or IPAc (compare Entries 1 and 7 and Entries 2, 3 and 8). When lower CO (P(CO) 2 bar, Entry 10, Table 2) or catalyst loadings (2.5 mol%, Entry 14, Table 2) were tested, the influence of the activating agent became relevant in the overall yield of (**VI**) recovered at the end of the reaction (compare Entries 4–6 and 10, 14, Table 2). Finally, different diphosphine ligands (DPPP and DPPE) and a monophosphine (PPh_3) were tested (Figure 1) (Entries 15–17, Table 2).

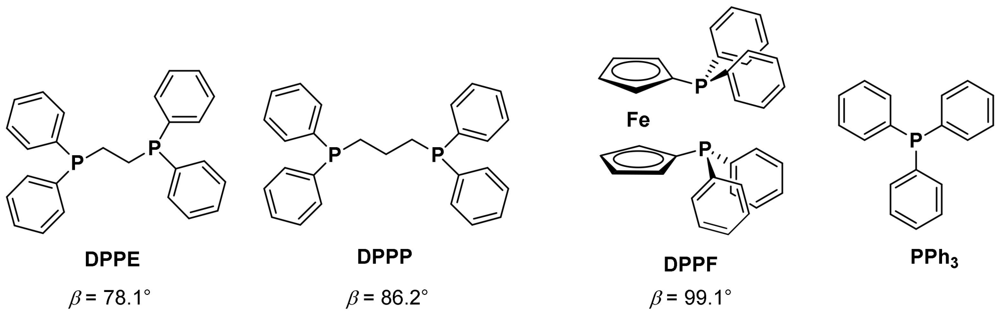
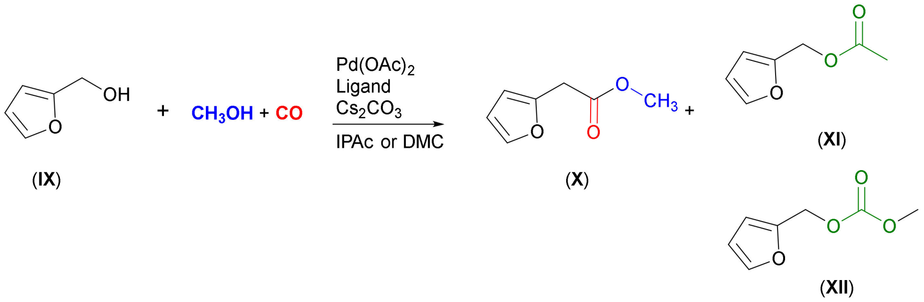


Figure 1. Phosphine ligands evaluated in this study for one-pot methoxycarbonylation reactions. Natural bite angle (β) reported are taken from ref. [51].

Data reported in Table 2 show that at P(CO) 5 bar, T 130 °C in the presence of 5 mol% Cs_2CO_3, 5 mol% $Pd(OAc)_2$ and $Pd(OAc)_2$/Ligand = 1/2 (mol/mol), both DPPP and DPPE gave high substrate conversions but relatively modest yields in (**VI**) (Entries 15 and 16, Table 2). Respectively, over 26% and 57% of intermediate benzo[d][1,3]dioxol-5-ylmethyl acetate (**VII**) were also present in the reaction mixture after 18 h. As previously reported in the literature, this may be a consequence of the different diphosphine bite angles [8,52]. It is in fact known that when catalysts bearing chelating diphosphine ligands are used, the natural bite angle of the ligand backbone may considerably modify the electronic and steric properties of the metal complex influencing its reactivity [51–55]. Data reported in Table 2 are perfectly in line with this hypothesis since the best-performing ligand (DPPF) has a wider bite angle (99.1°), giving a quantitative conversion of (**V**) both in the presence of DMC and IPAc (Entries 2, 4–6 and 8, Table 2). On the contrary, DPPP and DPPE with, respectively, a bite angle of 86.2° and 78.1° gave high conversions but modest yields in (**VI**), confirming their lower reactivity in equivalent reaction conditions. For the sake of completeness, triphenylphosphine (PPh_3) was also tested since it is largely employed as a ligand in carbonylation reactions. However, in agreement with the literature [8], the use of PPh_3 was detrimental both in terms of the catalyst activity and yield (Entry 17, Table 2).

2.3. *One-Pot Methoxy Carbonylation of Furfuryl Alcohol (**IX**)*

Data collected from the one-pot methoxycarbonylation of benzyl alcohol and piperonyl alcohol demonstrate the efficacy of $Pd(OAc)_2$/DPPF in the presence of an activating agent (IPAc or DMC) and a base for the direct synthesis of the corresponding acetate; thus, further experiments were carried out starting from biomass-derived furfuryl alcohol (**IX**) to widen the scope of the synthetic strategy devised (Scheme 5).



Scheme 5. Methoxycarbonylation of furfuryl alcohol (**IX**).

Surprisingly, adopting the best reaction conditions as reported above, in the presence of DPPF as a ligand and DMC or IPAC as an activating agent, only modest yields in (**X**) were achieved (75% and 77%, respectively) after 18 h at 130 °C, together with 20% and 4%, respectively, of intermediate furan-2-ylmethyl acetate (**XI**) and furan-2-yl-methyl methyl carbonate (**XII**) (Entries 1 and 2, Table 3).

Table 3. Methoxycarbonylation of furfuryl alcohol (**IX**) in different reaction conditions.

Entry [a]	A [b]	Ligand	T (°C)	t (h)	Conv (%) [c]	Yield (X) (%) [c]
1	DMC	DPPF	130	18	95	75
2	IPAc	DPPF	130	18	81	77
3	DMC	DPPE	130	18	62	10
4	IPAc	DPPE	130	18	80	18
5	DMC	DPPP	130	18	99	95
6	IPAc	DPPP	130	18	92	90
7	DMC	DPPP	130	1	94	85
8 [d]	DMC	DPPP	130	18	99	98
9	IPAc	DPPP	100	18	99	70
10	DMC	DPPP	100	4	95	93
11 [d]	DMC	DPPP	80	18	99	95
12	DMC	DPPP	80	18	95	84
13	IPAc	DPPP	80	18	92	55

[a] Reaction conditions: (**IX**) = 1 mmol; MeOH = 1.0 mL, P(CO) = 5 bar, Cs_2CO_3 = 20 mol%. [b] Activating agent, DMC = 1.5 mL, IPAc = 1.0 mL. [c] Substrate conversion and product yield were calculated by GC analysis using mesitylene as an internal standard. Differences between conversions and product yield correspond to the percentage of intermediate present in the reaction mixture. [d] P(CO) = 20 bar.

Thus, further experiments were carried out in the presence of DPPE and DPPP in a 2/1 ratio with respect to $Pd(OAc)_2$. In agreement with data reported above for (**V**), also in this case, DPPE gave very poor results both in the presence of DMC or IPAc (Entries 3 and 4, Table 3), while DPPP allowed to achieve high yields in the desired product in the presence of either activating agents (Entries 5 and 6, Table 3). These results seem to indicate that not only the bite angle of the bidentate ligand but also the nature of the substrate significantly influence the activity of the catalytic system. Further experiments are ongoing to gain deeper insight into the mechanism of the one-pot methoxycarbonylation.

Finally, a set of experiments was carried out at lower reaction temperatures (down to 80 °C) and variable P(CO) (between 5 and 20 bar), showing that for T 80 °C, a higher P(CO) is necessary to recover (**X**) in yields above 90% (compare Entries 11 and 12, Table 3), while at higher temperatures (130 °C), the CO pressure can be lowered down to 5 bar, without any consequence on the conversion and yield in (**X**) (compare Entries 5 and 8, Table 3).

3. Materials and Methods

3.1. Materials

Commercial solvents (Aldrich) were purified as described in the literature [56]. Reagents were commercially available compounds and were used as received unless otherwise stated. $Pd(OAc)_2$ was purchased from Sigma Aldrich (St. Louis, MO, USA), while $Pd(TFA)_2$ and $Pd(DPPF)Cl_2$ x Acetone were provided by Strem Chemicals (Newburyport, MA, USA). DPP (P, DPPE and PPh_3 were provided by Sigma Aldrich. DPPF was provided by Strem Chemicals. Benzyl, piperonyl and furfuryl alcohol were also purchased from Sigma Aldrich. High-purity CO was obtained from SIAD.

3.2. Instrumentation

The ^1H and ^{13}C NMR spectra were registered on a Bruker AVANCE 300 spectrometer operating at 300.1 and 75.44 MHz, respectively. Gas–liquid chromatography (GLC) analyses were performed on an Agilent 6850 gas chromatograph; gas chromatography–mass spectrometry (GC–MS) analyses were performed on an HP 5890 series II gas chromatograph interfaced to a HP 5971 quadrupole mass detector.

3.3. Generic Procedure for One-Pot Methoxycarbonylation

As an example, the experimental procedure for the methoxycarbonylation of benzyl alcohol (**I**) (Entry 1, Table 1) is reported.

Under an inert atmosphere, in a 25 mL vial equipped with a magnetic bar, MeOH (1.0 mL), $Pd(OAc)_2$ (5 mol%, 0.05 mmol), and DPPF (10 mol%, 0.1 mmol) were introduced. Then, under nitrogen, benzyl alcohol (**I**) (1 mmol), Cs_2CO_3 (5 mol%, 0.05 mmol), and IPAc (1.5 mL) were added, obtaining a reddish solution. Finally, the vial was placed in a pre-purged 150 mL autoclave and 50 bar of CO was added. The autoclave was then heated at 130 °C and kept under constant magnetic stirring. After 18 h, the autoclave was cooled to room temperature, and the residual gas was carefully vented off. The raw reaction mixture was analysed by GLC to determine the substrate conversion and product composition. The reaction crudes were purified by flash chromatography (silica gel, 60 Å, 70–230 mesh, and a 1:1 mixture of ethylacetate and n-hexane) to give methyl 2-phenylacetate (**II**).

3.4. Product Characterisation

Methyl 2-phenylacetate (**II**) [8,57]: Colourless oil. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.67 (s, 2H), 3.69 (s, 3H), 7.40–7.29 (m, 5H). ^{13}C NMR (75.44 MHz, $CDCl_3$) δ (ppm) = 41.5, 52.4, 127.4, 129.0, 129.6, 134.4, 171.7. GC-MS: m/z = 150 [M]+, 91, 65.

Benzyl acetate (**III**) [58]: Colourless oil. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.11 (s, 3H), 5.12 (s, 2H), 7.33–7.38 (m, 5H); ^{13}C NMR (75.44 MHz, $CDCl_3$) δ (ppm) = 20.9, 66.2, 128.2, 128.5, 135.9, 170.8. GC-MS: m/z= 150 [M]+, 109, 108, 91, 90, 79, 77.

Benzyl methyl carbonate (**IV**) [59]: Colourless oil. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.80 (s, 3H), 5.17 (s, 2H), 7.34–7.39 (m, 5H); ^{13}C NMR (75.44 MHz, $CDCl_3$) δ (ppm) = 54.7, 69.5, 128.2, 128.4, 128.5, 135.2, 155.6; GC-MS (EI): m/z 166 [M]+.

Methyl 2-(benzo[d][1,3]dioxol-5-yl)acetate (**VI**) [60]: Colourless oil. ^1H NMR (300 MHz; $CDCl_3$) δ (ppm) = 3.53 (s, 2H), 3.69 (s, 3H), 5.93 (s, 2H), 6.68–6.78 (m, 3H); 13C NMR

(75.44 MHz; $CDCl_3$) δ (ppm) = 40.8, 52.1, 101.0, 108.3, 109.7, 122.4, 127.5, 146.7, 147.8, 172.1; GC-MS: m/z = 194 [M]+, 135, 77.

Benzo[d][1,3]dioxol-5-ylmethyl acetate (**VII**) [61]: Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.11 (s, 3H), 5.03 (s, 2H), 5.98 (s, 2H), 6.93–6.74 (m, 3H); ^{13}C NMR (75.44 MHz, $CDCl_3$) δ (ppm) = 21.3, 66.5, 101.4, 108.5, 109.3, 122.5, 129.9, 147.9, 148.0, 171.1; GC-MS: m/z = 194 [M]+.

Benzo[d][1,3]dioxol-5-ylmethyl methyl carbonate (**VIII**): GC-MS: m/z = 196 [M]+, 77.

Methyl 2-(fur-2-yl)acetate (**X**) [25]: Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.69 (s, 2H), 3.71 (s, 3H), 6.22 (d, 1H), 6.33 (dd, 1H), 7.35 (d, 1H). ^{13}C NMR (75.44 MHz, $CDCl_3$) δ (ppm) = 33.8, 52.2, 108.0, 110.5, 142.0, 147.5, 169.8; GC-MS: m/z = 140 [M]+, 81.

Furan-2-ylmethyl acetate (**XI**) [62]: Colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 1.92 (s, 3H), 4.90 (s, 2H), 6.21 (m, 1H), 6.25 (d, 1H), 7.27 (m, 1H); ^{13}C NMR (75.44 MHz, $CDCl_3$) δ (ppm) = 20.8 58.0, 110.5, 110.6, 143.3, 149.4, 170.7; GC-MS: m/z = 140.0 [M]+.

Furan-2-yl-methyl methyl carbonate (**XII**) [63]: Yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 3.79 (s, 3H), 5.12 (s, 2H), 6.36 (dd, 1H), 6.46 (d, 1H,), 7.43(dd, 1H).^{13}C NMR (75.44 MHz, $CDCl_3$): δ 155.54, 148.70, 143.54, 111.28, 110.58, 61.35, 54.93. GC-MS: m/z = 156.0 [M]+.

4. Conclusions

In summary, in this paper, a sustainable and straightforward method for the one-pot synthesis of alkyl arylacetates and furanyl acetates via Pd-catalysed methoxycarbonylation has been reported. The procedure reported allows the obtainment of key compounds in organic synthesis in one step, without the use of a halogenated substrate or mineral acids and from readily available and economic starting reagents.

In this paper, $Pd(OAc)_2$/DPPF, in the presence of IPAc or DMC as an activating agent and an inorganic base, has been verified to be an optimal catalytic system for the methoxycarbonylation of arylalkyl alcohols (benzyl and piperonyl alcohol) at P(CO) pressures as low as 2 bar, at 30 °C for 18 h, with conversions and yields in the desired acetates above 90%. Interestingly, a reduction in P(CO) favourably affected the catalyst activity and selectivity towards the desired product, probably due to a competing effect in the coordination of CO and the substrate on the metal centre at higher P(CO) pressures. Adversely, when methoxycarbonylation of furfuryl alcohol was performed in similar conditions to benzyl alcohols, $Pd(OAC)_2$/DPPF was not very efficient and a different diphosphine (DPPP) had to be used to achieve high yields in (**X**).

In conclusion, the synthesis of alkylaryl acetates and furfuryl acetate was carried out from the corresponding alcohols, avoiding the use of halogen containing salt or strong acids, employing a safe activating agent (IPAc and DMC) without the need for complicated purification steps. Further mechanistic investigations are currently ongoing to understand the activity of the catalyst system towards different substrates and in the presence of different ligands.

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