ChemPubSoc Europe

DOI: 10.1002/ejoc.201901592

EurJOC European Journal of Organic Chemistry

Full Paper

Carbonylation

# Palladium-Catalyzed Alkoxycarbonylation of *sec*-Benzylic Ethers

Carolin Schneider,[a] Ralf Jackstell,[a] Bert U. W. Maes,[b] and Matthias Beller*[a]

**Abstract:** Herein, we report the palladium-catalyzed synthesis of 3-arylpropionate esters starting from secondary benzylic ethers. With this investigation it could be shown that ethers are suitable starting materials in addition to the established carbonylation reactions of olefins, alcohols, or aryl halides.

## Introduction

Homogeneous catalytic carbonylation reactions are known for more than 80 years. Already in 1938, Otto Roelen discovered the synthesis of aldehydes from alkenes and syngas (hydroformylation), while he was trying to transfer the Fischer–Tropsch synthesis into the industrial scale.[1] Shortly after, Walter Reppe introduced carbonylations of alkynes and related chemistry.[2]

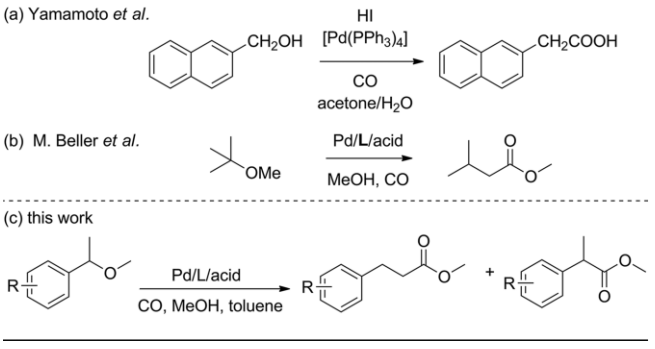
Already in early years, these practical methodologies were successfully introduced into industrial applications and today especially hydroformylations represent the largest process in homogeneous catalysis. In addition to aldehydes generated in the oxo process,[3] methyl methacrylate is industrially realized from methoxycarbonylation of ethylene in the so-called Lucite α process.[4] Furthermore, in this context the Monsanto[5] or Cativa[6] processes have to mentioned, too. In both cases acetic acid is produced on bulk ton-scale starting from methanol and CO.

Over the years and especially from the academic point of view various carbonylation reactions (e.g. hydroformylation,[7] hydroxycarbonylation,[8] alkoxycarbonylation[9] or aminocarbonylation[10]) became an important tool and a straight-forward method to produce all kinds of carboxylic acid derivatives. For these reactions olefins,[11] alcohols[12] or aryl halides[13] constitute standard starting materials and a large range of products such as esters, acids, aldehydes, amides, and alcohols can be efficiently accessed.[14,15]

Among the different types of olefins, terminal[9,11] and internal[16] as well as sterically hindered and demanding alkenes were studied.[17] These studies go along with finding ways to improve the catalyst activity and/or controlling the (regio)selectivity which often is regulated by the corresponding ligand systems.

While in the past most industrial and academic efforts were on the carbonylation of olefins, recently there is an increasing interest in the synthesis of carboxylic acid derivatives from *sec*- and *tert*-alcohols,[12] partly because of their availability from renewables. Due to their increased reactivity, benzylic and allylic alcohols have been investigated mainly in the past. Notable examples for palladium-catalyzed carbonylation of allylic alcohols were disclosed by the groups of Alper and Miura as well as ours.[18] Here, the specific catalyst system in both cases was based on $Pd(OAc)_2$ and $PPh_3$ and showed superior performance to give β,γ-unsaturated carbonyl compounds. Similar studies regarding the carbonylation of benzyl alcohol and its analogues have been achieved. In the latter case, the reactions often proceed through the corresponding benzyl halides.[19] Furthermore, it is to mention that Ibuprofen is produced on multi-ton scale from the corresponding secondary benzylic alcohol via carbonylation.[20] For both substrates the in situ generated benzylic and allylic intermediates are highly stabilized, which enables easier C–O bond cleavage.

Compared to alcohol carbonylations, similar transformations applying ethers as starting material are much less explored. A notable exception is the use of methyl *tert*-butyl ether (MTBE), an important industrial bulk chemical and a representative for *tert*-ethers (Scheme 1b).[17]




Scheme 1. Carbonylation of (a) benzylic alcohol, (b) methyl *tert*-butyl ether, and (c) this work, secondary benzylic ethers.

[a] *Leibniz-Institut für Katalyse e.V. ,*
*Albert-Einstein Straße 29a, 18059 Rostock, Germany*
*E-mail: matthias.beller@catalysis.de*
*www.catalysis.de*
[b] *University of Antwerp,*
*Groenenborgerlaan 171, 2020 Antwerp, Belgium*

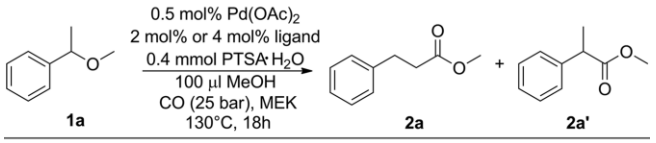
*Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejoc.201901592.*

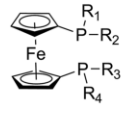
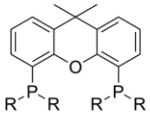
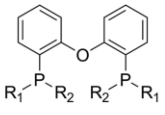
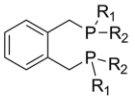
Based on our continuous interest in carbonylation, we became attracted to explore the palladium-catalyzed carbonylation reaction of benzyl ethers as starting material (Scheme 1c). Herein, we show that those *sec*-ethers allow for efficient preparation of 3-arylpropionate. In general, they show comparable performance to the established carbonylation reactions of olefins, alcohols, and aryl halides. We believe these findings will broaden the substrate class scope in carbonylation chemistry.

## Results and Discussion

In the past three years, we developed specific phosphine ligands with so-called built-in-base function for various palladium-catalyzed alkoxycarbonylations.[21] Explicit incorporation of *tert*-butyl and pyridine substituents on the phosphorus atom of several bidentate phosphine ligands enhanced the rate of the nucleophilic attack on the intermediate palladium acyl complex.[22] Hence, we were interested in the behavior of such ligands in the carbonylation of ethers.

At the beginning of our investigations, different $Pd(OAc)_2$/ligand combinations were tested for secondary benzylic ether carbonylation reactions using (1-methoxyethyl)benzene as the model substrate. In this benchmark reaction, 0.5 mol-% $Pd(OAc)_2$ was used as catalyst precursor in the presence of 2 or 4 mol-% of a bi- or monodentate phosphorus ligand, respectively, in methylethylketone (MEK) as solvent. To ensure complete esterification 2.5 equivalents of methanol were added. In general, the mixture was heated at 130 °C for 18 hours at 25 bar of CO pressure (Scheme 2).



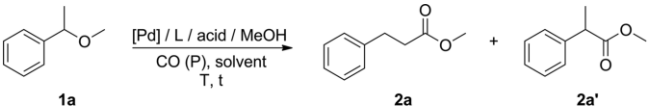

| Ligand | | Yield (l/b) |
|---|---|---|
| no ligand | - | 0 % |
|  | **L1**: $R_1$=$R_2$=$R_3$=$R_4$ = $^t$Bu | < 1 % (n.a.) |
| | **L2**: $R_1$=$R_2$ = Ph $R_3$=$R_4$ = $^t$Bu | 5 % (n.a.) |
| | **L3**: $R_1$=$R_4$= $^t$Bu $R_2$=$R_3$ = 2-py | 21 % (79/21) |
| | **L4**: $R_1$=$R_2$=$R_3$=$R_4$ = Ph | 46 % (81/19) |
|  | **L5**: R = $^t$Bu | <1 % (n.a.) |
| | **L6**: R= Ph | 67 % (83/17) |
|  | **L7**: $R_1$=$R_2$ = $^t$Bu | 2 % (n.a.) |
| | **L8**: $R_1$= Ph $R_2$=$^t$Bu | 34 % (91/10) |
| | **L9**: $R_1$=$R_2$ = Ph | 58 % (84/16) |
|  | **L10**: $R_1$=$R_2$ = $^t$Bu | <1 % (n.a.) |
| | **L11**: $R_1$= $^t$Bu $R_2$= 2-py | 54 % (85/15) |
|  | **L12**: $R_1$= Ph $R_2$= 2-py | 5 % (n.a.) |
| | **L13**: $R_1$=$R_2$ = Ph | 16 % (81/19) |

Scheme 2. Palladium-catalyzed carbonylation of (1-methoxyethyl)benzene: investigation of different phosphine ligands. Reaction conditions: 1.0 mmol **1a**, 0.5 mol-% $Pd(OAc)_2$, 2 mol-% L (bidentate) or 4 mol-% (monodentate) ligand, PTSA·$H_2O$ (0.4 mmol), 100 µL MeOH, 2 mL methylethylketone (MEK), 130 °C, 25 bar CO, 18 h. Yields were determined by GC analysis using hexadecane as internal standard. Selectivity's are obtained by GC analysis, but due to the measurement error range not for yields ≤ 5 %.

This systematic ligand screening pointed out the strong influence of the substituents at the phosphorus atoms. Independent from the core structure, ligands with bis-di-*tert*-butylphosphino groups resulted in nearly no product formation. A stepwise substitution of the *tert*-butyl substituents by phenyl or 2-pyridyl groups increased the formation of **2a** (4–45 %) and **2a′** (1–8 %) significantly. Bidentate ligand patterns which only contained phenyl substituents like **L4** (dppf), **L6** (Xantphos), and **L9** (DPEphos) led to the highest yields (46, 67, and 58 %, respectively) under these conditions. Interestingly, the regioselectivities only slightly changed to give preferentially linear product **2a**. It is worthwhile to mention that bidentate ligands gave improved results compared to the standard monodentate phosphines.

With these results in hand, we continued the optimization of our reaction conditions (Pd source, acid, and ligand) (Table 1). Xantphos (**L6**) as ligand was first tested in combination with several palladium precursors, i.e. Pd-halides (Br, Cl) (entry 2), $Pd(dba)_2$ (entry 3), and $Pd(cod)X_2$ (X = Br, Cl) (entry 4) were compared. Notably, the use of $Pd^0$ as catalyst precursor lowered the yield to 36 %, even so no reduction of the palladium center was necessary. In case of tested $Pd^{II}$ sources there was no further influence observed and the yield of the desired product was around 70 % in total.

Table 1. Palladium-catalyzed carbonylation of (1-methoxyethyl)benzene: optimization of the reaction conditions.




| Entry[a] | Ligand | Pd source | Acid | Yield [%] (l/b) |
|---|---|---|---|---|
| 1 | **L6** | - | PTSA·$H_2O$ | 0 |
| 2 | **L6** | $PdX_2$ (X= Br, Cl) | PTSA·$H_2O$ | 70 (83/17) |
| 3 | **L6** | $Pd(dba)_2$ | PTSA·$H_2O$ | 36 (83/17) |
| 4 | **L6** | $Pd(cod)X_2$ (X= Br, Cl) | PTSA·$H_2O$ | 66 (82/18) |
| 5 | **L6** | $Pd(OAc)_2$ | PTSA·$H_2O$ | 67 (83/17) |
| 6[b] | **L4** | $Pd(OAc)_2$ | PTSA·$H_2O$ | >99 (81/19) |
| 7[b] | **L6** | $Pd(OAc)_2$ | PTSA·$H_2O$ | >99 (83/17) |
| 8[b] | **L9** | $Pd(OAc)_2$ | PTSA·$H_2O$ | >99 (80/20) |
| 9[b] | **L9** | $Pd(OAc)_2$ | – | 0 |
| 10[b] | **L9** | $Pd(OAc)_2$ | TFA | 0 |
| 11[b] | **L9** | $Pd(OAc)_2$ | pyridinesulfonic acid | 0 |
| 12[b,c] | **L9** | $Pd(OAc)_2$ | PTSA·$H_2O$ | 13 (79/21) |
| 13[b,d] | **L9** | $Pd(OAc)_2$ | PTSA·$H_2O$ | >99 (84/16) |
| 14[b,e] | **L9** | $Pd(OAc)_2$ | PTSA·$H_2O$ | 66 (83/17) |
| 15[b,f] | **L9** | $Pd(OAc)_2$ | PTSA·$H_2O$ | 90 (83/17) |

[a] Reaction conditions: 1.0 mmol (1-methoxyethyl)benzene, 0.5 mol-% palladium precursor, 2 mol-% **L6**, 0.3 mmol PTSA·$H_2O$, 100 µL MeOH, 2 mL MEK, 130 °C, 25 bar CO, 18 h. [b] Reaction conditions: 2 mol-% **L**, 0.3 mmol acid, 2 mL toluene. [c] Reaction conditions: 100 °C. [d] Reaction conditions: 160 °C. [e] Reaction conditions: 10 bar. [f] Reaction conditions: 40 bar. Yields were calculated via GC analysis using hexadecane as internal standard.

Next, the influence of the palladium loading was studied under our benchmark conditions. Here, different catalyst concentrations between 0.25–3.00 mol-% were tested. Surprisingly, no significant influence was detected (yields: 60–70 %) (data Table S1 ESI). This behavior could also be observed for different Pd:Xantphos ratios. While testing ratios between 1 and 6 equivalents, the product yield varied in-between 60 % to 70 % (data Table S2 ESI). Finally, variation of the solvent proved to be crucial for the improvement of the reaction system. While performing the reaction exclusively in methanol, the ether **1a** is not consumed at all. However, in toluene the yield of 2a and 2a′ could be improved to ≥ 99 % in the presence of L4 (dppf), **L6** (Xantphos), and **L9** (DPEphos) (Table 1, entries 6–8). All further studies were performed using the least expensive DPEphos (**L9**) because ester yields were comparable in the presence of the most active ligands (**L4**, **L6**, and **L9**).

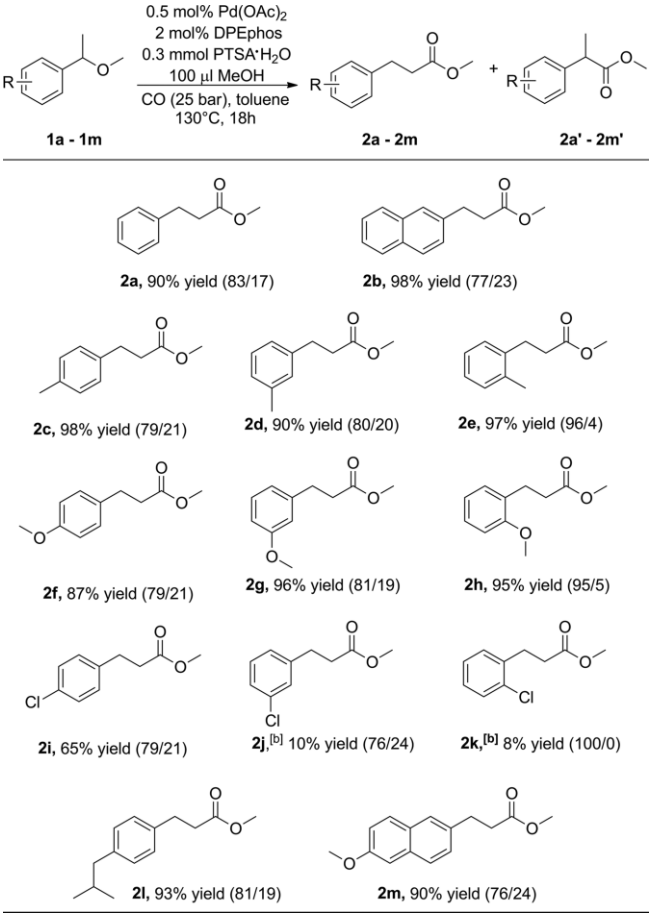
To allow for ether cleavage an acidic co-catalyst has to be added (entry 9). Among the tested acids, PTSA·$H_2O$ exclusively gave the desired reaction in moderate to excellent yields depending on the amount, while trifluoroacetic acid and pyridinesulfonic acid did not show any reaction (Table 1, entries 8–11). In case of PTSA·$H_2O$, amounts of 0.3–0.4 mmol Led to optimal results. Finally, the dependence of temperature, and pressure were investigated. While at lower temperature (100 °C) or pressure (10 bar) the catalyst activity dropped (entries 12, 14), comparable product yields were obtained at 160 °C or 40 bar CO (entries 13, 15).

With optimized reaction conditions, the scope of the reaction was studied (Table 2). The naphthalene analogue **1b** of the model compound was selectively transformed to **2b** and isolated in good yield. Similarly, diverse benzylic ethers, which are substituted on the aromatic ring with methyl- (**1c**–**1e**), methoxy- (**1f**–**1h**), or chloride (**1i**–**1k**) in *ortho*-, *meta*- and *para*-position, respectively, could be transformed. While the methyl- (**2c**–**2e**) and the methoxy- (**2f**–**2h**) substituted products were isolated in good to excellent yields, the *ortho*- and *meta* chloride-substituted compounds **2j** and **2k** resulted in nearly no product formation. In contrast, the 1-chloro-4-(1-methoxyethyl)benzene (**1i**) showed less inhibition and yielded **2i** in 65 %.

Besides, the carbonylation of 1-isobutyl-4-(1-methoxyethyl)-benzene (**1l**), which contains the core structure of ibuprofen, and of 2-methoxy-6-(1-methoxyethyl)-naphthalene (**1m**), as a part of the core structure of naproxen, were explored. To our delight, both relevant substrates were transformed to the desired products (**2l** and **2m**) and could be isolated in good yields (93 and 90 %). %). In addition, (1-methoxypropyl)benzene was successfully tested according to the possibility of forming an internal olefin as well as providing the option of isomerization (SI, S3).

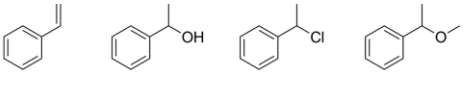
Encouraged by these results and to understand the mechanism of this carbonylation process, we compared the reactivity of different benzylic derivatives and styrene under identical reaction conditions. Apart from our model substrate (1-methoxyethyl)benzene and the corresponding olefin (styrene), 1-phenylethanol as well as (1-chloroethyl)benzene were tested in the presence of the optimal catalyst system at three different temperatures (Table 3).

Table 2. Palladium-catalyzed carbonylation of *sec*-benzylic ethers: substrate scope.[a]




[a] Unless otherwise noted, all reactions were performed in toluene (1.5 mL) at 130 °C for 18 h with **1** (1.0 mmol), $Pd(OAc)_2$ (1.12 mg, 0.5 mol-%), PTSA·$H_2O$ (0.3 mmol), **L9** (10.7 mg, 0.02 mmol), 100 µL MeOH, and CO (25 bar). The yields were isolated yields for the linear and branched mixture by column chromatography and the ratio of isomers was determined by GC analysis [linear/branched]. [b] Non-isolated yields, determined by GC analysis [linear/branched] using hexadecane as internal standard.

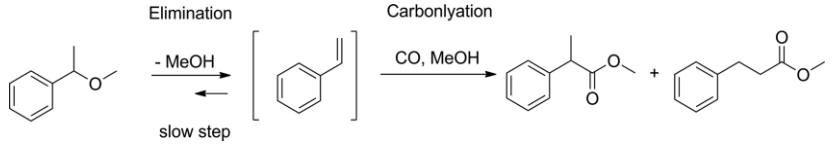
Table 3. Comparison of palladium-catalyzed carbonylations of benzylic derivatives and styrene.[a]




| Entry | Temperature [°C] | Olefine | Alcohol | Halide | Ether |
|---|---|---|---|---|---|
| 1 | 100 | > 99% [77/23] | 16% [76/24] | 23% [82/18] | 13% [79/21] |
| 2 | 130 | > 99% [80/20] | > 99% [82/18] | > 99% [79/21] | > 99% [83/17] |
| 3 | 160 | > 99% [81/19] | > 99% [84/16] | > 99% [72/28] | > 99% [84/16] |

[a] Reaction conditions: 1.0 mmol reaction scale, 0.5 mol-% $Pd(OAc)_2$, 2 mol-% DPEphos, PTSA·$H_2O$ (0.3 mmol), 100 µL MeOH, 2 mL toluene, 25 bar CO, 18 h. Yields were determined by GC analysis [linear/branched] using hexadecane as internal standard.

At 130–160 °C the reactivity for all substrates is comparable. In addition, similar regioselectivities are observed except for the




Scheme 3. Reaction pathway for the carbonylation of (1-methoxyethyl)-benzene under the established reaction conditions.

benzylic chloride, which gave slightly more of the branched ester. However, at lower temperature (100 °C), styrene turned out to be the most reactive substrate.

As a final point, the time-dependent conversion of styrene and (1-methoxyethyl)benzene under similar reaction conditions was compared. As shown in Figure 1, styrene is fully consumed within the first 90 min to give 90–95 % of the desired ester product (linear and branched).

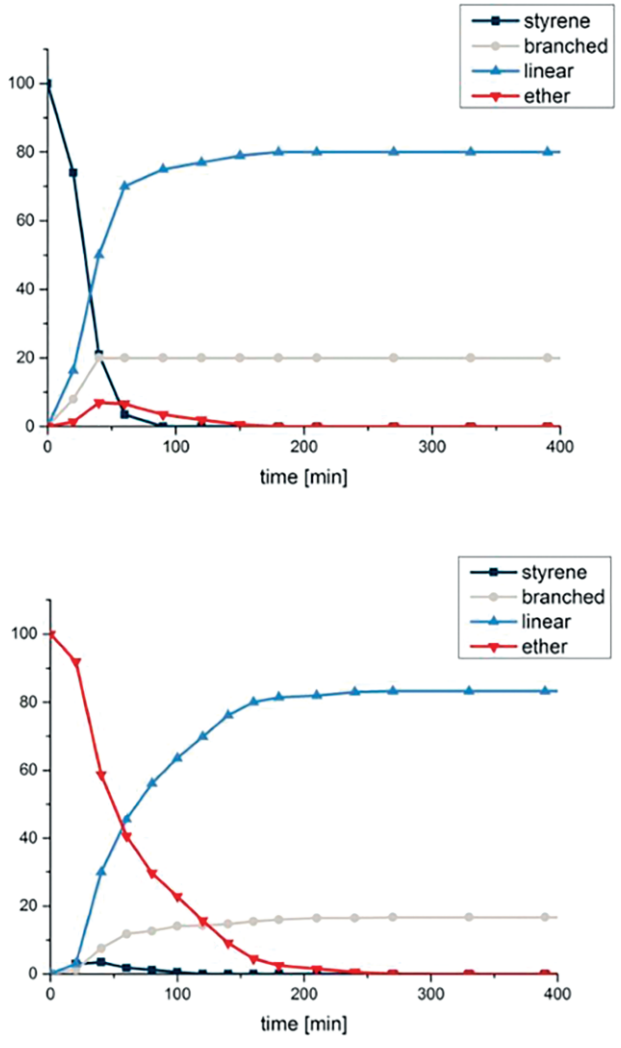



Figure 1. Kinetic investigations of styrene (upper) and (1-methoxyethyl)benzene (lower) under the established conditions (20 mL toluene at 130 °C with substrate (10.0 mmol), $Pd(OAc)_2$ (0.5 mol-%), PTSA·$H_2O$ (3.0 mmol), **L9** (2 mol-%), 1 mL MeOH, and CO (25 bar)).

The remaining product is the corresponding methyl ether, which is observed due to the added methanol in the reaction. Then, the cleavage of the ether is the limiting reaction step. The whole process is finished within 180 min. In contrast using 1a, full conversion needs a longer reaction time (270 min). Interestingly, in the first phase of the reaction small amounts of styrene can be observed here, too. This indicates this reaction is proceeding through styrene as an intermediate.

Based on all these studies as well as previous mechanistic investigations, we propose the following reaction pathway for the carbonylation of benzylic ethers (Scheme 3). Initially, acid-catalyzed elimination of methanol produces styrene, which is an intermediate in this reaction. Then final product is formed from styrene via the palladium-catalyzed carbonylation of the unsaturated carbon–carbon double bond. The elimination step is rate-determining in this process.

## Conclusions

In conclusion, we have shown that benzylic ethers can be used in carbonylation reactions analogous to the corresponding alcohols or styrenes. In the past, such ethers have been scarcely investigated. We clearly demonstrate that their reactivity in carbonylations is similar to styrenes, benzylic alcohols and benzylic halides. Optimal results are obtained with catalyst systems containing $Pd(OAc)_2$ precatalyst, and DPEphos or dppf or Xantphos as ligand, and PTSA as acid additive. With this method, further valorizations of benzylic ethers including renewable substrates can be envisioned.

## Experimental Section

### General considerations

All manipulations were carried out under an argon atmosphere using Schlenk-techniques, unless stated otherwise. All glass devices used for synthesis were dried and cooled under vacuum before use. Chemicals were purchased from commercial sources and used as received, if not stated otherwise. Oxygen-free and dry solvents were prepared by distillation or using a solvent purification system by Innovative Technologies.

Catalytic experiments were performed in 4 mL screw cap vials, closed with a polytetrafluoroethylene (PTFE)/white rubber septum (Wheaton 13 mm Septa) and phenolic cap. The connection with the atmosphere was achieved by a needle. The vials were placed inside a 300 mL Parr autoclave and stirred with a magnetic stirring bar.

### General ether preparation

All ethers were prepared starting from the corresponding alcohol or the ketone according to the general procedures.

Procedure 1, reducing the ketone to an alcohol: Reactions took place in a round-bottomed flask that had been charged with the ketone (1 equiv.) and was dissolved in THF. Further $NaBH_4$ (2 equiv.) was dissolved in water, and this solution was added to the THF dropwise whilst stirring at room temperature. The final solution was

stirred for 6 h, HCl was added to the reaction system. To accelerate the phase separation $H_2O$ was used and the aqueous phase was extracted by ether. Organic phases were combined and anhydrous $Na_2SO_4$ was used to remove the residual water. The desired alcohol was obtained after the solvents were removed under reduced pressure.

Procedure 2 conversion alcohols to ether: Reactions took place in a round bottom flame-dried Schlenk flask and flushed with argon three times. NaH (1.3 equiv.) was added and dissolved in anhydrous THF. The flask was placed in an ice bath to cool and stirred for 15 minutes. The desired alcohol (1 equiv.) was added dropwise and the solution was stirred for an additional hour. Then MeI (0.98 equiv.) was added in a dropwise fashion at low temperature. The solution was stirred at room temperature for 6 h and the remaining NaH was quenched with methanol. The product was obtained after extraction with a water and ether mixture (1:1), drying with $Na_2SO_4$ and removing the solvent under reduced pressure.

**Catalytic experiments**

In a typical catalytic experiment, the reaction were performed in 4 mL glass vials charged with $Pd(OAc)_2$ (0.5 mol-%), DPEphos (2.0 mol-%) and PTSA·$H_2O$ (0.3 mmol) rapidly weighed in the air. If used, solid substrates (1 mmol) were also weighed in the air and added into the vial. The atmosphere in the vial was then changed to argon and 1.5 mL toluene and 100 μL MeOH were added. Next, liquid substrates (1.0 mmol) were added and the vials were placed in a metal plate inside a 300 mL autoclave. The reactor was closed and pressurised with nitrogen (about 10 bar), which was released again. This was carried out two times, before the same procedure was done three times with CO (about 10 bar). After the last release the autoclave was pressurised with 25 bar CO and then heated to 130 °C for 18 h inside an aluminium block. At the end of the reaction the autoclave was placed into an ice bath to cool down and stop the reaction. Finally, the pressure was released, the reactor flushed with $N_2$ and opened.

## Conflicts of interest

There are no conflicts to declare.

## *Acknowledgments*

Financial support from Research Foundation Flanders (FWO) (BioFact Excellence of Science project Grant No. 30902231) and the Francqui Foundation is gratefully acknowledged.

**Keywords:** Carbonylation · Benzylic ethers · Palladium · Esters · Carbon monoxide

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Received: October 29, 2019