



# CO and H<sub>2</sub> gas-free efficient reductive carbonylation of aryl iodides. Use of smart recyclable metal-based catalysts

Nicolò Bosello<sup>a</sup>, Alessandro Di Michele<sup>b</sup>, Oreste Piccolo<sup>c,\*</sup>, Stefano Paganelli<sup>a,\*</sup>

<sup>a</sup> Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, Mestre, 30172 Venezia, Italy

<sup>b</sup> Dipartimento di Fisica e Geologia, Università degli Studi di Perugia, Via Pascoli, 06123 Perugia, Italy

<sup>c</sup> Studio di Consulenza Scientifica (SCSOP), Via Bornò 5, 23896 Sirtori, LC, Italy

## ARTICLE INFO

### Keywords:

Heterogeneous catalysis  
Carbonylation  
Aldehyde  
Fine chemicals  
Fragrance

## ABSTRACT

In this paper, we studied an efficient protocol of reductive carbonylation of two aryl iodides, namely 2-iodo-5-ethylthiophene and 5-iodobenzo[d][1,3] dioxole, employing formic acid, propylphosphonic anhydride (T3P) and a base, to afford aldehydes used as such as industrial flavors/fragrances or as key intermediates for some APIs and other fragrances. Our approach, comparing to the previously described protocol [1], not only avoids the use of unsafe reagents and/or solvents but, noteworthy, uses easily prepared heterogeneous catalysts with a low content of metal(s), such as 0.3 % Pd/Al<sub>2</sub>O<sub>3</sub>, (0.18 % Pd, 0.44 % Cu)/Al<sub>2</sub>O<sub>3</sub> and 1 % Cu/Al<sub>2</sub>O<sub>3</sub>. These catalysts, as well as commercial Pd/C species tested here for a comparison, are also recyclable and have been characterized before and after use by FE-SEM, EDS and TEM spectroscopy. Noteworthy, both the bimetallic system Pd-Cu/Al<sub>2</sub>O<sub>3</sub>, containing a very low amount of expensive palladium (0.18 %) and Cu/Al<sub>2</sub>O<sub>3</sub>, containing no palladium at all, showed very high activities.

## 1. Introduction

In a recent work, we presented and discussed the state of the art of the synthesis of aromatic and heteroaromatic aldehydes [2–24], and a quite sustainable protocol for the preparation of this type of products was identified on two model substrates of industrial interest. As a matter of fact, optimized reductive carbonylation on two iodo aryl and heteroaryl derivatives, using CO and silanes, in the presence of palladium-based recyclable catalysts, was successfully carried out [2]. However, the employment of pressurized CO may represent a serious drawback: it is an unsafe gas and can require considerable investment costs, thus limiting its use only to industries having a suitable equipment. Therefore, CO, and also H<sub>2</sub>, gas-free carbonylations could offer an applicability to a broad number of industries. Moreover, some carbon monoxide surrogates are easily transportable and available from waste biomass (e.g., paraformaldehyde, methanol, oxalates, formates etc.) [8, 24, 25]. Recently, a palladium-catalyzed CO-free carbonylative procedure for the synthesis of aromatic aldehydes from aryl iodides was described [1]. Formic acid, used as syngas surrogate, requires both CO and H<sub>2</sub> to be generated, so decomposition pathways must occur under

the reaction conditions. This was made possible by activation of formic acid with propylphosphonic anhydride (T3P). This last reagent is commercially available at industrial level and can be solubilized in different solvents. It is often employed as a reagent for the conversion of carboxylic acids into their derivatives such as esters and amides, to convert amides into nitriles, in the oxidation of alcohols, in C-C coupling reactions and in the synthesis of alkenes [26]. Noteworthy, the produced by-product propylphosphonic acid, could stabilize the active palladium center and make the addition of a phosphine ligand not necessary. Moreover, it is easily removed in the work-up, being water soluble. However, the previous protocol [1] had two relevant drawbacks: i) the best used solvent was DMF, that is a no more acceptable reaction medium, being a potent liver toxin and probably a carcinogenic agent [27]; ii) a homogeneous catalyst, such as palladium acetate, was employed. Disappointingly, no attempt to reuse it or to recover the precious metal was described [1]. Spurred by the interesting results described [1], we decided to identify a more sustainable procedure using 2-iodo-5-ethylthiophene (I) and 5-iodobenzo[d][1,3] dioxole (II) as model substrates to obtain 5-ethylthiophen-2-carbaldehyde (III) and piperonal (IV), respectively (Scheme 1). These aldehydes are used either as industrial

\* Corresponding authors.

E-mail addresses: [orestepiccolo@tin.it](mailto:orestepiccolo@tin.it) (O. Piccolo), [spag@unive.it](mailto:spag@unive.it) (S. Paganelli).

<sup>1</sup> <https://orcid.org/0000-0001-8948-2218>.

<sup>2</sup> <https://orcid.org/0000-0003-2116-3389>.

flavors/fragrances of commercial interest [28,29] or as key intermediates for the preparation of some APIs [30] and of other fragrances [31].

## 2. Experimental section

### 2.1. General

2-Iodo-5-ethylthiophene (I) and 5-iodobenzo[d][1,3]dioxole (II) were prepared as previously described [2,32]. 50 % Solutions of T3P in different solvents were received from Curia Germany GmbH (Germany). Different anhydrous 5 % Pd/C and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were received from Chimet S. p.A. (Italy). 0.3 % Pd/Al<sub>2</sub>O<sub>3</sub>, (0.18 % Pd, 0.44 % Cu)/Al<sub>2</sub>O<sub>3</sub> and 1 % Cu/Al<sub>2</sub>O<sub>3</sub> were prepared in a one pot procedure, as better described below, inspired by a reported procedure [2,33]. All the other reagents were Aldrich products. The quantitative analysis of the metals present in home-made catalytic systems was carried out by means of measurements of atomic absorption on a Perkin Elmer Analyst 100 spectrometer with a mono lamp hollow cathode element (Pd). Furthermore, some quantitative measurements of the metals were carried out using MP-AES (Microwave Plasma - Atomic Emission Spectrometer), on Agilent Technologies 4210. GC analyses were carried out on an Agilent 6850 A gas chromatograph (FFAP column 30 m x 0.25 mm x 0.25  $\mu$ m) and GC-MS analyses were performed by using an Agilent Technologies 7820 A GC System coupled with quadrupole mass spectrometer Agilent Technologies 5977B MSD (HP-5MS column 30 m x 0.25 mm x 0.25  $\mu$ m). As concerning the obtained results, we analysed the amount of the reaction products and the conversion degree of the starting materials by suitable calibration lines, using hexadecane as standard, with an uncertainty lower than 5 %.

### 2.2. Preparation of low metal content catalysts on alumina

#### 2.2.1. Preparation of Pd/Al<sub>2</sub>O<sub>3</sub> [2,33]

In a glass test tube, 26 mg (0.15 mmol) of PdCl<sub>2</sub>, 20 ml of cyclopentyl methyl ether (CPME), 0.22 ml (0.50 mmol) of trioctyl amine (TOA) and 5 g of alumina type 49 (Chimet) were introduced. Three vacuum-nitrogen cycles were then performed. The test tube was placed in a steel autoclave by flushing nitrogen, and subsequently 0.1 MPa of H<sub>2</sub> were loaded. The autoclave was maintained at 50 °C under stirring for 24 h and then, the gases were discharged. The gray solid was filtered, under nitrogen, on gooch and washed first with CPME and then with *n*-hexane; the solid was then dried under vacuum. The solid catalyst was analysed to determine the content of Palladium finding 0.3 % Pd/Al<sub>2</sub>O<sub>3</sub>. It was stored in a nitrogen atmosphere, before the use.

#### 2.2.2. Preparation of Pd-Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/Al<sub>2</sub>O<sub>3</sub> [2]

(0.18 % Pd, 0.44 % Cu)/Al<sub>2</sub>O<sub>3</sub> was obtained following the above-described procedure but using 2.5 mg (0.071 mmol) of PdCl<sub>2</sub>, 27.9 mg (0.282 mmol) of CuCl, 10 ml of CPME, 0.25 ml (0.56 mmol) of TOA, 2.5 g of alumina type 49 (Chimet) and 0.5 MPa of H<sub>2</sub>. 1 % Cu/Al<sub>2</sub>O<sub>3</sub> was obtained using 15.6 mg (0.158 mmol) of CuCl, 15 ml of CPME, 0.23 ml (0.527 mmol) of TOA, 1 g of alumina type 49 (Chimet) and 0.5 MPa of H<sub>2</sub>.

### 2.3. Characterization of catalysts

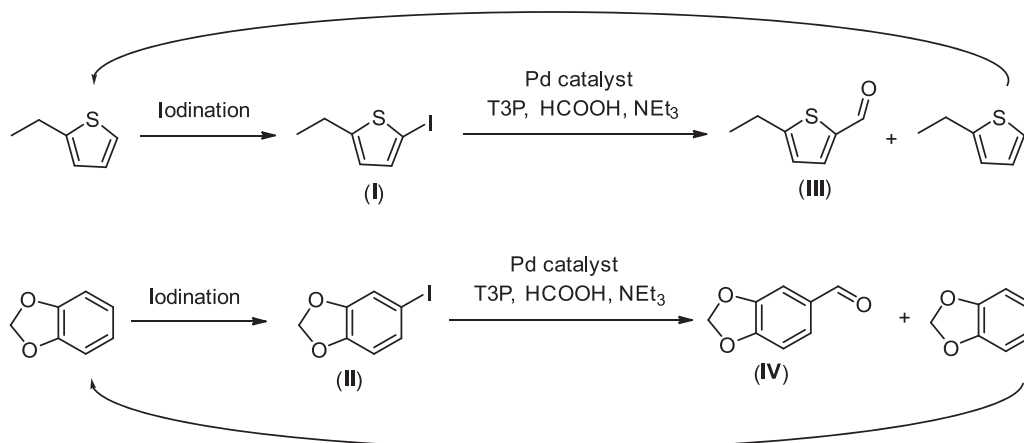
The morphology and composition were examined by Field Emission Gun Electron Scanning Microscopy (FE-SEM) LEO 1525 ZEISS. Elemental composition and chemical mapping were determined using Bruker Quantax EDS. TEM images were obtained using a Philips 208 Transmission Electron Microscope. The samples were prepared by putting one drop of an ethanol dispersion of the catalyst powder on a copper grid pre-coated with a Formvar film and dried in air. The characteristics of the catalysts are presented in Section 3 (Results and Discussion).

### 2.4. General procedure for the synthesis of 5-ethylthiophene-2-carbaldehyde (III) and piperonal (IV)

In the reactor, under inert atmosphere, the catalyst of choice, substrate (I) or (II) solubilized in acetonitrile, formic acid, 50 % of T3P solution and TEA were introduced in the ratios reported in the Plots. The order in which the reagents are added is important, as the base once added to the reactive environment develops effervescence. Once closed, the reactor was connected to a thermostat at the predetermined reaction temperature and the mixture was maintained under magnetic stirring. After the reaction time required for the test, the equipment was cooled down quickly and the reaction gases produced were vented. The heterogeneous catalyst was removed by filtration and the mixture was introduced into a separating funnel together with an aqueous supersaturated sodium chloride solution. The organic phase was separated, dried over sodium sulphate and filtered. The reaction mixture was analysed by gas chromatography, using hexadecane as internal standard. The aldehydes (III) and (IV) were characterized by <sup>1</sup>H NMR and by GC-MS. The results were in agreement with the literature data [34,35].

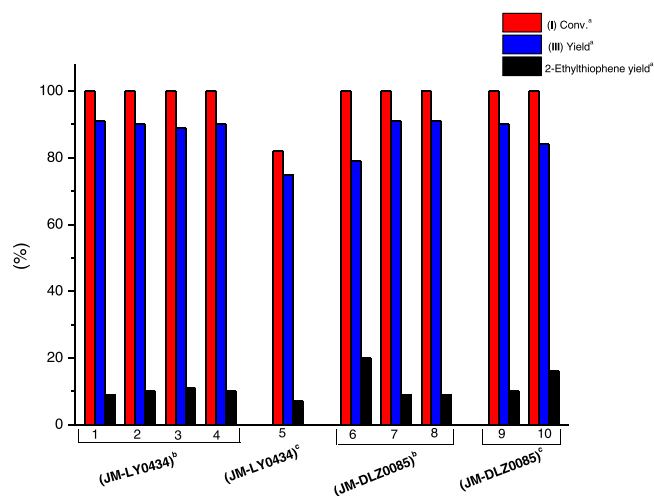
**Compound (III)** [34]: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 9.74 (s, 1 H, COH), 7.54 (d, 1 H, *J* = 3.7 Hz), 6.85 (d, 1 H, *J* = 3.7 Hz), 2.84 (q, 2 H, *J* = 7.5 Hz), 1.27 (t, 2 H, *J* = 7.5 Hz). *m/z*: 140 [M]<sup>+</sup>, 125[M - CH<sub>3</sub>]<sup>+</sup>, 111[M - HCO]<sup>+</sup>, 97 [M - CH<sub>3</sub>CH<sub>2</sub>HCO]<sup>+</sup>.

**Compound (IV)** [35]: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.8 (s, 1 H, CHO), 7.43 (dd, 1 H, *J*<sub>1</sub> = 7.9 Hz, *J*<sub>2</sub> = 1.6 Hz), 7.35 (d, 1 H, *J* = 1.6 Hz), 6.95 (d, 1 H, *J* = 7.9 Hz), 6.10 (s, 2 H). MS (70 eV): *m/z*: 150 [M]<sup>+</sup>, 149

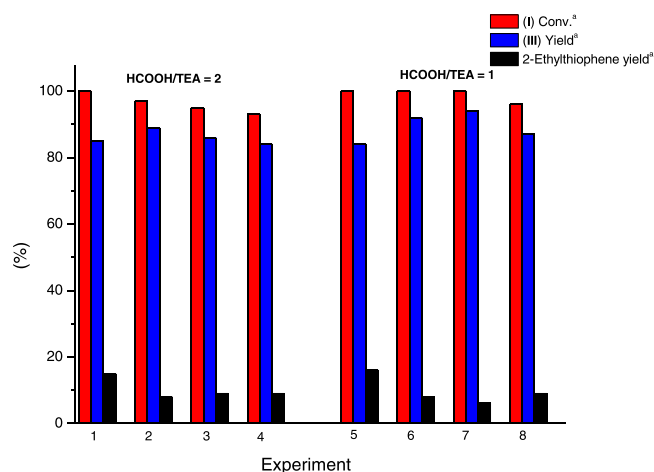


**Scheme 1.** 5-Ethylthiophen-2-carbaldehyde (III) and piperonal (IV) synthetic scheme.





**Plot 3.** Carbonylation of (I) catalyzed by some wet Pd/C catalysts in the presence of HCOOH, TEA and T3P (50 % in acetonitrile). Reaction conditions: substrate (I) = 238 mg (1 mmol); (I)/Pd (molar ratio) = 30/1; T = 100 °C; t = 24 h; Solvent (CH<sub>3</sub>CN) = 5 ml; Formic acid (4.5 mmol); T3P (0.8 mmol); HCOOH/TEA molar ratio = 2. <sup>a</sup> Determined by GC analysis, using hexadecane as standard. <sup>b</sup> Pre-activated catalyst with 0.1 MPa of H<sub>2</sub> at rt for 1 h in acetonitrile. <sup>c</sup> Not pre-activated catalyst with H<sub>2</sub>. Experiments 2, 3, 4, 7, 8 and 10 were carried out by using the catalyst recovered from the previous reaction.

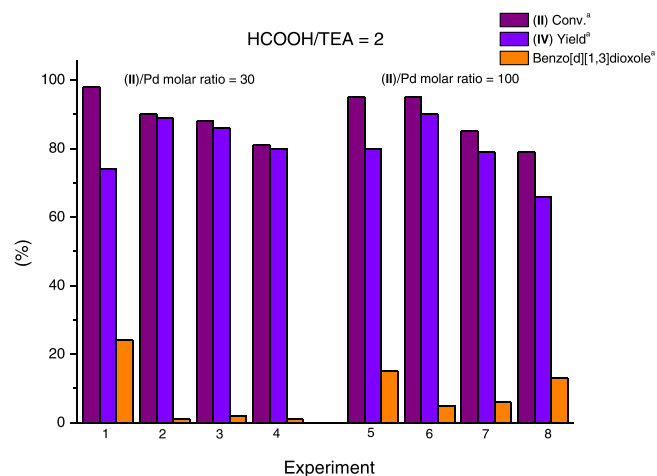


**Plot 4.** Carbonylation of (I) catalyzed by 5 % Pd/C (Chimet 1237 L) in the presence of HCOOH, TEA and T3P (50 % in acetonitrile). Reaction conditions: substrate (I) = 280 mg (1.18 mmol); (I)/Pd (molar ratio) = 100/1; Formic acid (4.5 mmol); T3P (0.8 mmol); T = 100 °C; t = 24 h; Solvent (CH<sub>3</sub>CN) = 5 ml. <sup>a</sup> Determined by GC analysis, using hexadecane as standard. Experiments 2–4 and 6–8 were carried out by using the catalyst recovered from the previous reaction.

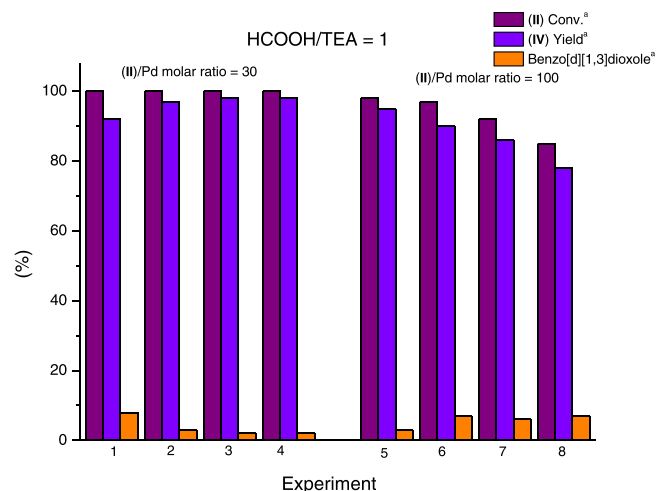
preactivated in a reducing atmosphere as in previous experiments.

Remarkably, the experiments carried out with the recycled catalyst, working with (II)/Pd (molar ratio) = 30/1, gave better results than with the fresh catalyst, especially with a HCOOH/TEA molar ratio equal to 1, affording the desired aldehyde with 98 % yield (exp. 2–4, Plot 6). Disappointingly, working with a lower catalyst amount, a progressive decrease of catalytic efficiency was noted both in terms of conversion and selectivity. We hypothesized that this could be probably due to a partial deactivation of the catalyst for metal particles aggregation or to a slight loss of the metal.

Recently, we prepared a new class of low metal content catalysts on alumina using an improved one-pot preparation [2,33]. We decided to explore the activity of these heterogeneous catalysts [0.3 % Pd/Al<sub>2</sub>O<sub>3</sub>,



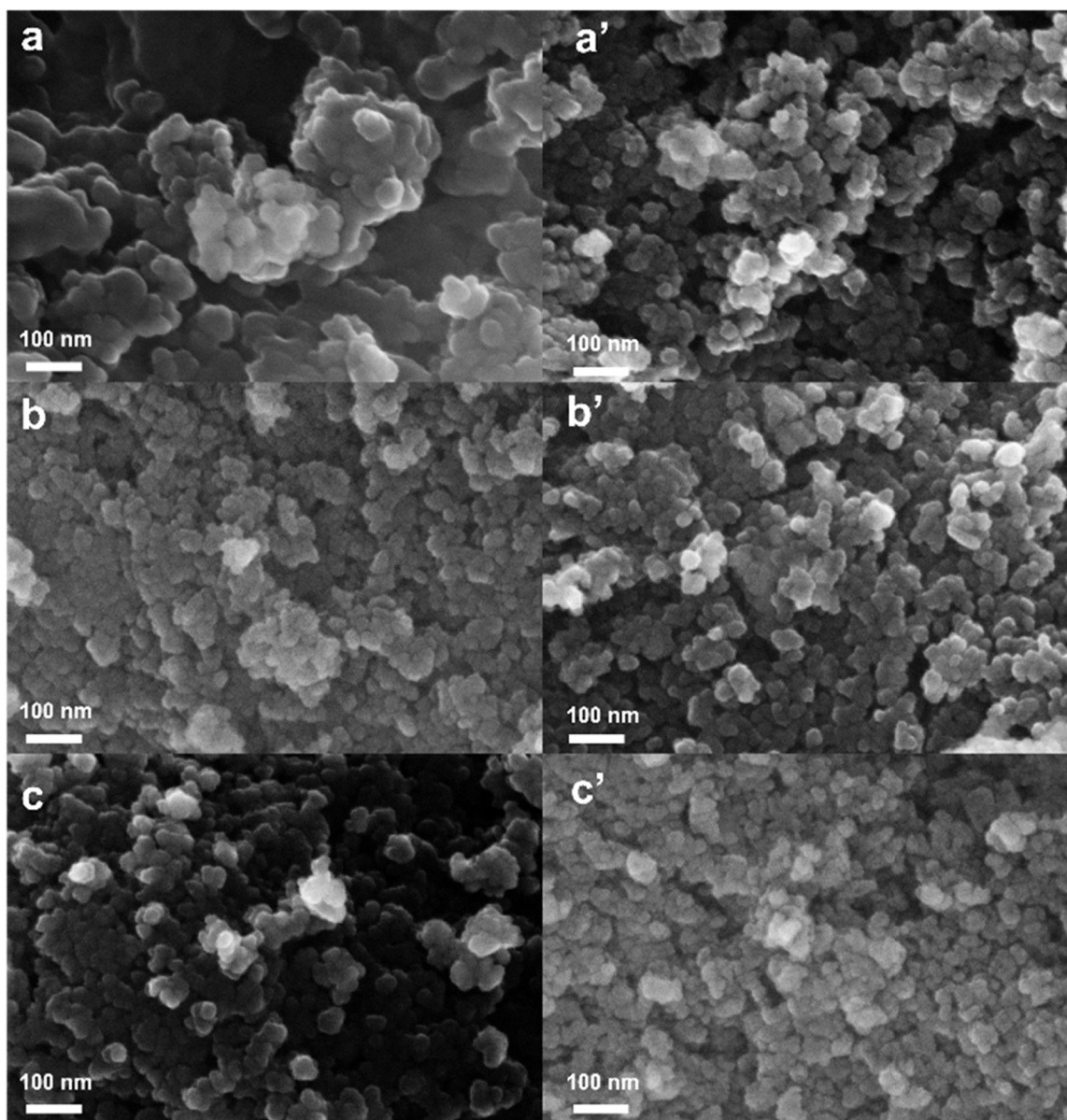
**Plot 5.** Carbonylation of (II) catalyzed by 5 % Pd/C (Chimet 1237 L) in the presence of HCOOH/TEA (molar ratio = 2) and T3P (50 % in acetonitrile). Reaction conditions: substrate (II) = 235 mg (0.95 mmol); T = 100 °C; t = 24 h; Solvent (CH<sub>3</sub>CN) = 5 ml; Formic acid (4.5 mmol); T3P (0.8 mmol); (II)/Pd (molar ratio) = 30/1 (exp. 1–4); (II)/Pd (molar ratio) = 100/1 (exp. 5–8); <sup>a</sup> Determined by GC analysis, using hexadecane as standard. Experiments 2–4 and 6–8 were carried out by using the catalyst recovered from the previous reaction.



**Plot 6.** Carbonylation of (II) catalyzed by 5 % Pd/C (Chimet 1237 L) in the presence of HCOOH/TEA (molar ratio = 1) and T3P (50 % in acetonitrile). Reaction conditions: substrate (II) = 235 mg (0.95 mmol); T = 100 °C; t = 24 h; Solvent (CH<sub>3</sub>CN) = 5 ml; Formic acid (4.5 mmol); T3P (0.8 mmol); (II)/Pd (molar ratio) = 30/1 (exp. 1–4); (II)/Pd (molar ratio) = 100/1 (exp. 5–8); <sup>a</sup> Determined by GC analysis, using hexadecane as standard. Experiments 2–4 and 6–8 were carried out by using the catalyst recovered from the previous reaction.

(0.18 % Pd, 0.44 % Cu)/Al<sub>2</sub>O<sub>3</sub> and 1 % Cu/Al<sub>2</sub>O<sub>3</sub>] in the carbonylation process. All these catalysts were not characterized before but now the fresh and used catalysts were studied by SEM and TEM electron microscopy and by EDX elemental mapping. The SEM images are shown in Fig. 1. They show that the sizes of the catalysts are less than 100 nm and with a lamellar structure. EDX analyses (Fig. 2) show the presence of Pd and Cu on the surface of the catalysts.

TEM images (Fig. 3) confirm the lamellar structure of Al<sub>2</sub>O<sub>3</sub> and highlight the presence of metal nanoparticles on support surface with dimensions less than 10 nm (indicated by arrows). SEM e TEM images demonstrated that the metal nanoparticles remain well dispersed on the support surface and do not aggregate after the reaction.



**Fig. 1.** SEM images of fresh catalysts a) 0.3 % Pd/Al<sub>2</sub>O<sub>3</sub>, b) (0.18 % Pd, 0.44 % Cu)/Al<sub>2</sub>O<sub>3</sub>, c) 1 % Cu/Al<sub>2</sub>O<sub>3</sub> and of corresponding used catalysts a') 0.3 % Pd/Al<sub>2</sub>O<sub>3</sub>, b') (0.18 % Pd, 0.44 % Cu)/Al<sub>2</sub>O<sub>3</sub>, c') 1 % Cu/Al<sub>2</sub>O<sub>3</sub>.

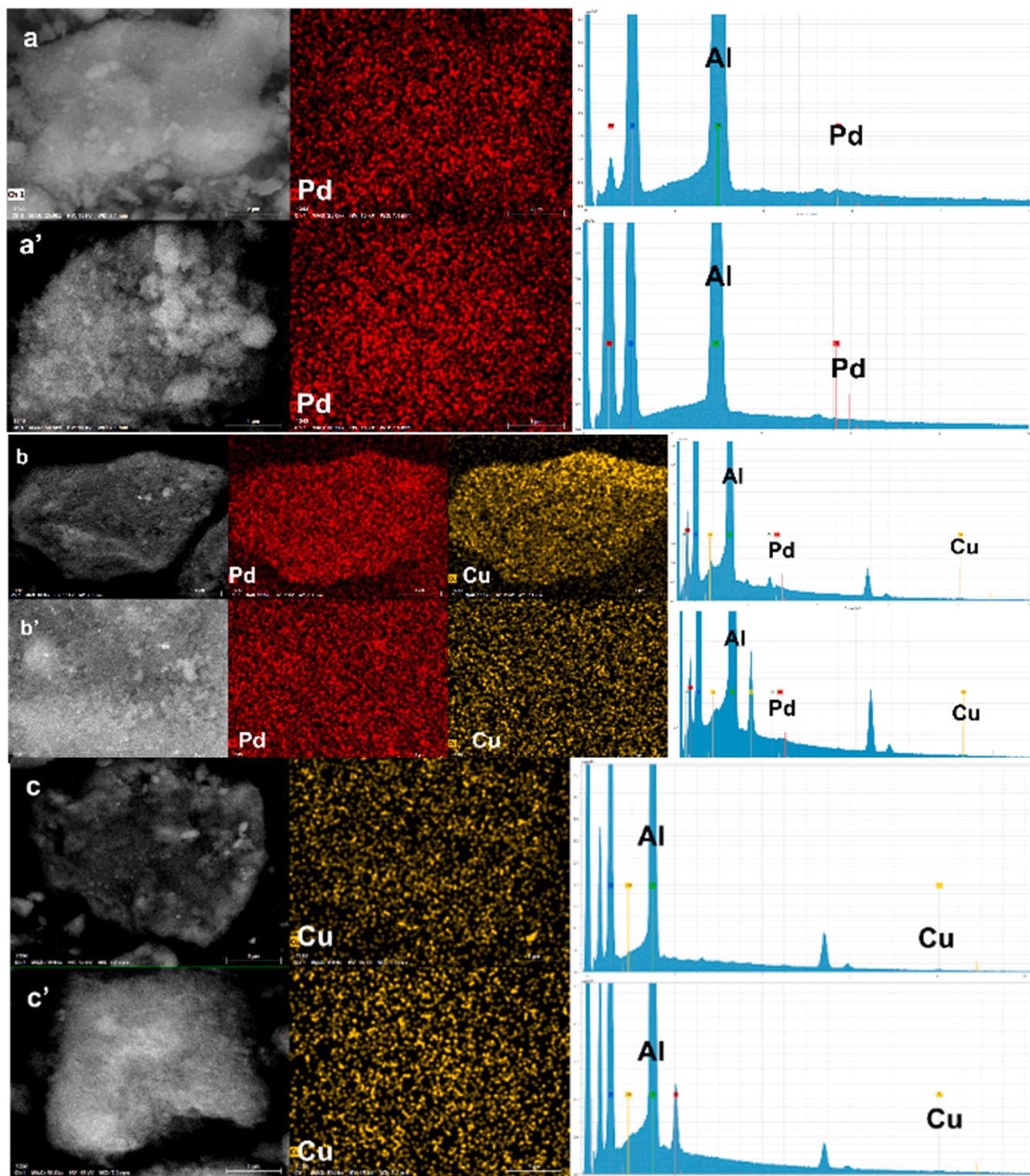
The carbonylation reactions were carried out on both substrates (I) and (II), and the results are shown in Plot 7 and Plot 8, respectively. Catalysts 0.3 % Pd/Al<sub>2</sub>O<sub>3</sub> was pre-activated with 0.1 MPa of H<sub>2</sub> at rt for 1 h in acetonitrile while catalysts (0.18 % Pd, 0.44 % Cu)/Al<sub>2</sub>O<sub>3</sub> and 1 % Cu/Al<sub>2</sub>O<sub>3</sub> were pre-activated with 2.0 MPa of H<sub>2</sub> always at rt for 1 h in acetonitrile. The treatment with H<sub>2</sub> was carried out at different pressure as it depends on the different capacity of the metals to be reduced.

All these catalysts gave comparable results with those obtained with commercial 5 % Pd/C catalysts but the advantage of using low metal content catalysts in terms of safety and sustainability must be emphasized, especially as regards the Pd-based catalysts. Noteworthy, when the bimetallic system Pd-Cu/Al<sub>2</sub>O<sub>3</sub> was used, despite the lower amount of palladium employed, the activity of the catalyst was very high, probably due to a synergic effect of the two metals, even if no metal alloy was formed. The low metal content and the use of a not precious metal as Cu represents a significant advantage in terms of cost-effectiveness and process safety. Even more surprising the results obtained in the presence of the only copper-based catalyst 1 % Cu/Al<sub>2</sub>O<sub>3</sub>. Although, it does not contain any precious metal, as checked by atomic absorption, excellent

conversions and aldehyde yields were obtained, especially in the case of substrate (I) (Plot 7). The results with the simple copper catalyst are particularly remarkable and deserve further study as they pave the way for an even more sustainable industrial process for these and other important aryl and heteroaryl aldehydes.

#### 4. Conclusions

Using two model substrates, having different steric and electronics properties, an improved synthesis of two industrially important aldehydic compounds was realized by reductive carbonylation of aryl- and heteroaryl iodo precursors, employing formic acid, propylphosphonic anhydride (T3P) and TEA as reagents. In comparison with the previous protocol reported in the literature [1], it was possible to avoid dangerous solvents and to use commercial or easily prepared heterogeneous recyclable mono- or bi-metallic catalysts, instead of homogeneous palladium acetate. It was also particularly significant the possibility: a) to improve the performances of palladium catalyst adding copper on alumina; b) to realize the synthesis using only copper as

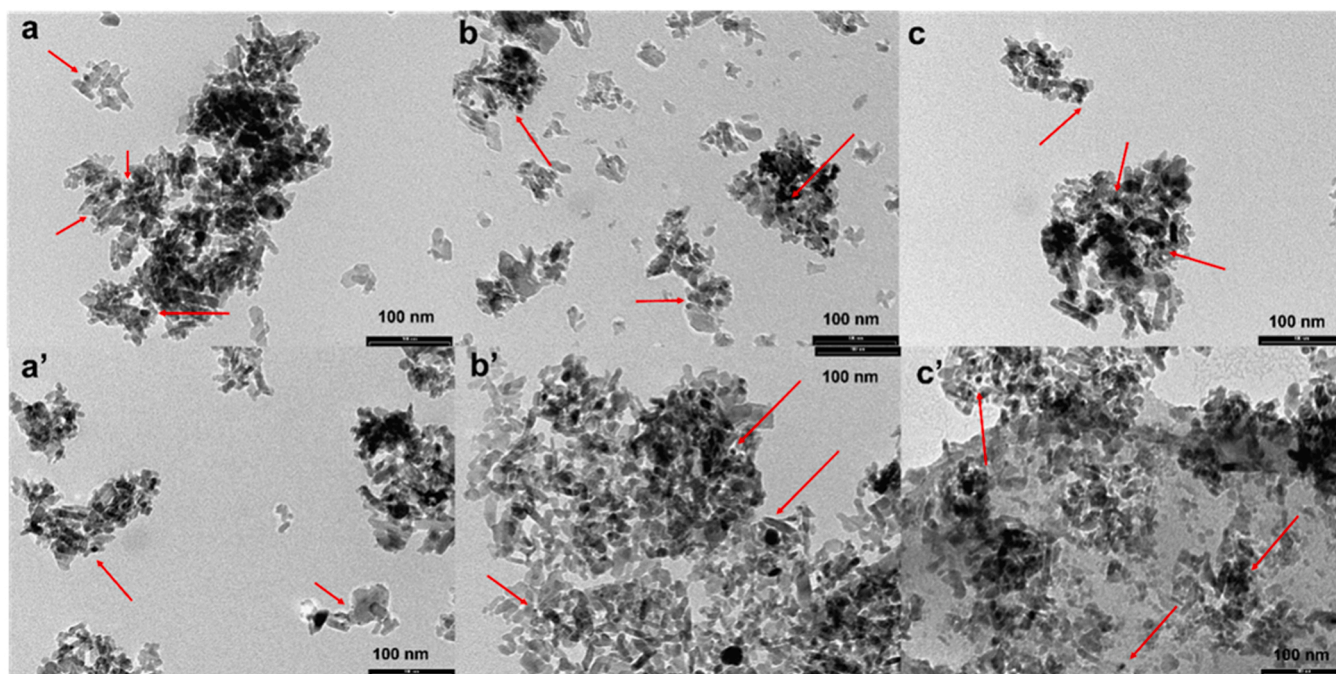


**Fig. 2.** EDX elemental mapping of fresh catalysts a) 0.3 % Pd/Al<sub>2</sub>O<sub>3</sub>, b) (0.18 % Pd, 0.44 % Cu)/ Al<sub>2</sub>O<sub>3</sub>, c) 1 % Cu/ Al<sub>2</sub>O<sub>3</sub> and of corresponding used catalysts a') 0.3 % Pd/ Al<sub>2</sub>O<sub>3</sub>, b') (0.18 % Pd, 0.44 % Cu)/ Al<sub>2</sub>O<sub>3</sub>, c') 1 % Cu/ Al<sub>2</sub>O<sub>3</sub>.

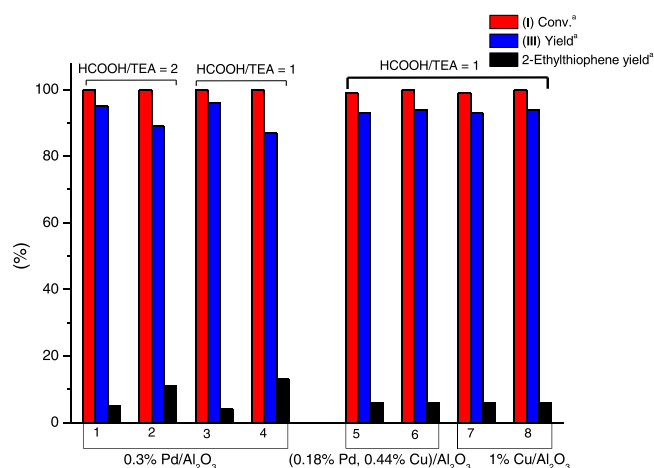
metallic catalyst, even if under more severe conditions. In perspective, this last procedure could represent a more sustainable preparative pathway of many other valuable aryl and heteroaryl aldehydes, possibly applicable on a large scale.

#### Funding

This work was supported by the institutional funding of Ca' Foscari University Venice [ADIR (Assegnazioni Dipartimentali per la Ricerca) 2021 and 2022)].



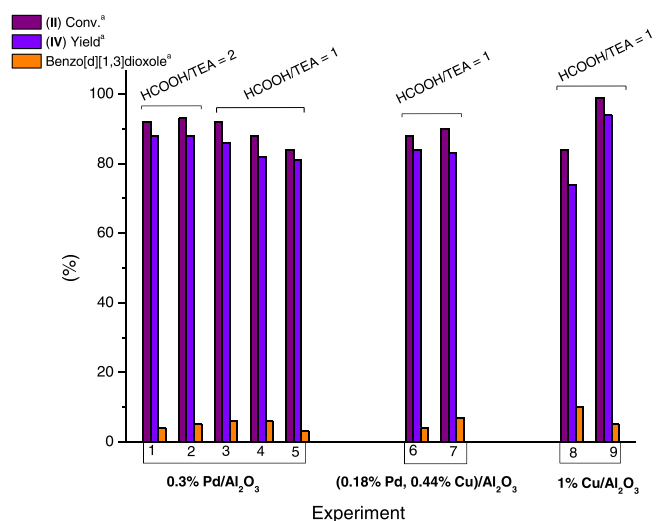
**Fig. 3.** TEM images of fresh catalysts a) 0.3 % Pd/Al<sub>2</sub>O<sub>3</sub>, b) (0.18 % Pd, 0.44 % Cu)/Al<sub>2</sub>O<sub>3</sub>, c) 1 % Cu/Al<sub>2</sub>O<sub>3</sub> and of the corresponding used catalysts a') 0.3 % Pd/Al<sub>2</sub>O<sub>3</sub>, b') (0.18 % Pd, 0.44 % Cu)/Al<sub>2</sub>O<sub>3</sub>, c') 1 % Cu/Al<sub>2</sub>O<sub>3</sub>.



**Plot 7.** Carbonylation of (I) catalyzed by some low metal content catalysts on alumina in the presence of HCOOH, TEA and T3P (50 % in acetonitrile). Reaction conditions: substrate (I) = 280 mg (1.18 mmol); (I)/Pd (molar ratio) = 100/1; Formic acid (4.5 mmol); T3P (0.8 mmol); T = 100 °C; t = 24 h; Solvent (CH<sub>3</sub>CN) = 5 ml. <sup>a</sup> Determined by GC analysis, using hexadecane as standard. Experiments 2–4, 6 and 8 were carried out by using the catalyst recovered from the previous reaction. Experiments 5 and 6: (I)/(Pd & Cu) (molar ratio) = 100/1 and T = 120 °C. Experiments 7 and 8: (I)/Cu (molar ratio) = 50/1 and T = 120 °C.

#### CRediT authorship contribution statement

**Nicolò Bosello:** Data curation, Investigation. **Alessandro Di Michele:** Methodology, Formal analysis, Investigation, Data curation, Supervision, Validation, Writing - original draft, Writing - review & editing. **Oreste Piccolo:** Investigation, Conceptualization, Data curation, Supervision, Validation, Writing - original draft, Writing - review & editing. **Stefano Paganelli:** Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Supervision, Funding acquisition, Project administration, Validation, Writing - original draft, Writing -



**Plot 8.** Carbonylation of (II) catalyzed by some low metal content catalysts on alumina in the presence of HCOOH, TEA and T3P (50 % in acetonitrile). Reaction conditions: substrate (II) = 293 mg (1.18 mmol); (II)/Pd (molar ratio) = 100/1; Formic acid (4.5 mmol); T3P (0.8 mmol); T = 120 °C; t = 24 h; Solvent (CH<sub>3</sub>CN) = 5 ml. <sup>a</sup> Determined by GC analysis, using hexadecane as standard. Experiments 2–5, 7 and 9 were carried out by using the catalyst recovered from the previous reaction. Experiments 6 and 7: (II)/(Pd & Cu) (molar ratio) = 100/1 and T = 120 °C. Experiments 8 and 9: (II)/Cu (molar ratio) = 50/1 and T = 120 °C.

review & editing.

#### Declaration of Competing Interest

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.

## Data availability

Data will be made available on request.

## Acknowledgements

We would like to thank Chimet SpA for kindly providing alumina and different 5 % Pd/Al<sub>2</sub>O<sub>3</sub>. We also thank Curia Germany GmbH for kindly providing 50 % solutions of T3P in different solvents.

## References

- [1] X.-F. Wu, *Sci. Rep.* 8 (2018) 8389–8393, <https://doi.org/10.1038/s41598-018-26850-2>.
- [2] S. Paganelli, R. Tassini, O. Piccolo (and loc. ref.), *Chem. Sel.* 7 (2022), e202202393, <https://doi.org/10.1002/slct.202202393>.
- [3] M.B. Smith, in: *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, eighth ed., Wiley, 2019, pp. 1439–1606.
- [4] C. Kohlpaintner, M. Schulte, J. Falbe, P. Lappe, J. Weber, in: *Ullmann's Encyclopedia of Industrial Chemistry*, first ed., John Wiley & Sons, Weinheim, 2000.
- [5] F. Aldabbagh, in: A.R. Katritzky, R.J.K. Taylor (Eds.), *Compr. Org. Funct. Group Transform.* II, Vol. 3, Elsevier Ltd, Amsterdam, 2005, pp. 9–133.
- [6] G. Pattenden, L.P. Crawford, S.K. Richardson, in: G. Pattenden (Ed.), *Gen. Synth. Method*, 16, Royal Society of Chemistry, 1994, pp. 37–91.
- [7] W. Kantlehner, *Eur. J. Org. Chem.* 14 (2003) 2530–2546, <https://doi.org/10.1002/ejoc.200200653>.
- [8] F.P. Wu, J.B. Peng, L.S. Meng, X. Qi, X.F. Wu, *ChemCatChem* 9 (2017) 3121–3124, <https://doi.org/10.1002/cctc.201700517>.
- [9] S.A.M.W. van den Broek, J.R. Leliveld, R. Becker, M.M.E. Delville, P.J. Nieuwland, K. Koch, F.P.J.T. Rutjes, *Org. Proc. Res. Dev.* 16 (2012) 934–938, <https://doi.org/10.1021/op2003437>.
- [10] M.A. Osman, *Helv. Chim. Acta* 65 (1982) 2448–2449, <https://doi.org/10.1002/hlca.19820650810>.
- [11] J.A. Peters, H. Van Bekkum, *Recueil* 100 (1981) 21–24, <https://doi.org/10.1002/recl.19811000106>.
- [12] T. Amakasu, K. Sato, *Bull. Chem. Soc. Jpn* 40 (1967) 1428–1432, <https://doi.org/10.1246/bcsj.40.1428>.
- [13] S. Klaus, H. Neumann, A. Zapf, D. Strbing, S. Hbner, J. Almerna, T. Riermeier, P. Grob, M. Sarich, W.-R. Krahnert, K. Rossen, M. Beller, *Angew. Chem. Int. Ed.* 45 (2006) 154–158, <https://doi.org/10.1002/anie.200502697>.
- [14] H. Neumann, R. Kadyrov, X.-F. Wu, M. Beller, *Chem. Asian J.* 7 (2012) 2213–2216, <https://doi.org/10.1002/asia.201200462>.
- [15] A.G. Sergeev, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* 130 (2008) 15549–15563, <https://doi.org/10.1021/ja804997z>.
- [16] A.S. Singh, J.M. Nagarkar, B.M. Bhanage, *Tetrahedron Lett.* 52 (2011) 2383–2386, <https://doi.org/10.1016/j.tetlet.2011.02.097>.
- [17] F.K. Sheffy, J.K. Stille, *J. Am. Chem. Soc.* 105 (1983) 7173–7175, <https://doi.org/10.1021/ja00362a027>.
- [18] V.P. Baillargeon, J.K. Stille, *J. Am. Chem. Soc.* 108 (1986) 452–461, <https://doi.org/10.1021/ja00263a015>.
- [19] I. Pri-Bar, O. Buchman, *J. Org. Chem.* 49 (1984) 4009–4011, <https://doi.org/10.1021/jo00195a026>.
- [20] Y. Misumi, Y. Ishii, M. Hidai, *Organometallics* 14 (1995) 1770–1775, <https://doi.org/10.1021/om00004a033>.
- [21] L. Ashfield, C.F. Barnard, *J. Org. Proc. Res. Dev.* 11 (2007) 39–43, <https://doi.org/10.1021/op060193w>.
- [22] A. Brennfuhrer, H. Neumann, M. Beller, *Angew. Chem. Int. Ed.* 48 (2009) 4114–4133, <https://doi.org/10.1002/anie.200900013>.
- [23] W. Han, B. Liu, J. Chen, Q. Zhou, *Synlett* 28 (2017) 835–840, <https://doi.org/10.1055/s-0036-1588930>.
- [24] T. Ueda, H. Konishi, K. Manabe, *Angew. Chem. Int. Ed.* 52 (2013) 8611–8615, <https://doi.org/10.1002/anie.201303926>.
- [25] O. Piccolo, S. Paganelli, *Carbon monoxide*, in: G. Bartolo (Ed.), *Organic Synthesis. Carbonylation Chemistry*, Wiley-VCH, Weinheim, 2021, pp. 149–195.
- [26] A.A. Waghmare, R.M. Hindupur, H.N. Pati, *Rev. J. Chem.* 4 (2014) 53–131, <https://doi.org/10.1134/S2079978014020034>.
- [27] J.-H. Yoon, C.-I. Yoo, Y.-S. Ahn, *Scand. J. Work Environ. Health* 45 (2019) 396–401, <https://doi.org/10.5271/sjweh.3802>.
- [28] (TGSC Information System). (<http://www.thegoodscentcompany.com/data/rw1043931.html>).
- [29] (TGSC Information System). (<http://www.thegoodscentcompany.com/data/rw1005891.html>).
- [30] X.-X. Shi, S.-L. Liu, W. Xu, Y.-L. Xu, *Tetrahedron Asymmetry* 19 (2008) 435–442, <https://doi.org/10.1016/j.tetasy.2007.12.017>.
- [31] (TGSC Information System). (<http://www.thegoodscentcompany.com/data/rw1007731.html>).
- [32] P. Lulinski, L. Skulski, *Bull. Chem. Soc. Jpn* 73 (2000) 951–956, <https://doi.org/10.1246/bcsj.73.951>.
- [33] S. Paganelli, A. Angi, N. Pajer, O. Piccolo, *Catalysts* 11 (2021) 14, <https://doi.org/10.3390/catal11010014>.
- [34] A.E. Aydin, *Appl. Organomet. Chem.* 27 (2013) 283–289, <https://doi.org/10.1002/aoc.2969>.
- [35] X. Jiang, J. Zhang, S. Ma, *J. Am. Chem. Soc.* 138 (2016) 8344–8347, <https://doi.org/10.1021/jacs.6b03948>.