



The Palladium-Catalyzed Carbonylative Telomerization Reaction with Phenols, Polyphenols and Kraft Lignin

Clément Dumont, Frederic Belva, Régis M. Gauvin, Mathieu Sauthier

► To cite this version:

Clément Dumont, Frederic Belva, Régis M. Gauvin, Mathieu Sauthier. The Palladium-Catalyzed Carbonylative Telomerization Reaction with Phenols, Polyphenols and Kraft Lignin. *ChemSusChem*, 2018, 11 (22), pp.3917-3922. <10.1002/cssc.201802017>. <hal-02107989>

HAL Id: hal-02107989

<https://hal.science/hal-02107989v1>

Submitted on 5 Dec 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

The Palladium-Catalyzed Carbonylative Telomerization Reaction with Phenols, Polyphenols and Kraft Lignin

C. Dumont,^{[a],[b]} F. Belva,^[b] R. M. Gauvin,^[a] M. Sauthier*^[a]

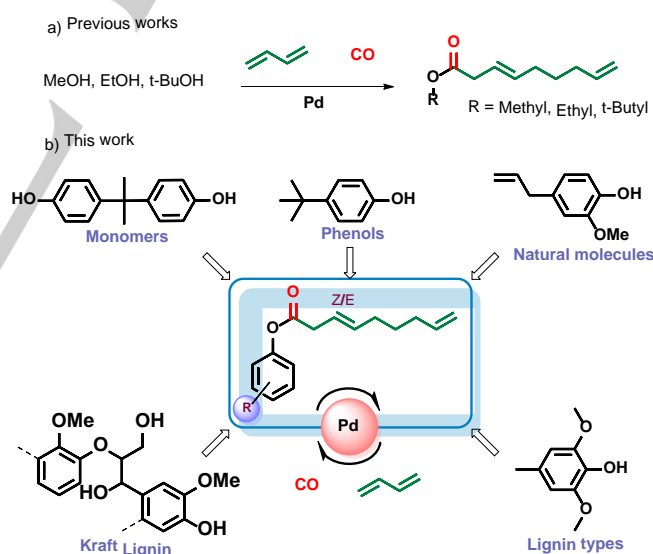
Dedication ((optional))

Abstract: The carbonylative coupling reaction of two equivalents of 1,3-butadiene is efficiently performed with phenols as nucleophile and yields aryl nona-3,8-dienoate esters. This transformation promoted by palladium-based catalysts has been optimized and this study evidences a key role of benzoic acid as co-catalyst. The use of this catalyst combination allowed the conversion of a wide scope of variously substituted phenols and the access to the corresponding esters with high yields. The reaction was further studied with diphenols, naturally-occurring phenols and an industrial grade Kraft lignin, thus broadening the scope of this reaction to the transformation of natural polyphenolic structures of industrial relevance.

Introduction

Metal-catalyzed carbonylation reactions^[1] are powerful tools for the multi-component synthesis of esters from alcohols, CO and an olefin^[2] or a diene.^[3] These reactions are highly atom-economical and involve starting materials that are readily accessible on very large scale. This synthetic advantage combined with the development of very active catalysts brought this family of reactions to the industrial scale, as in the case of methylpropionate synthesis from ethylene methoxycarbonylation. Alkoxy carbonylation reactions generally involve aliphatic alcohols or polyols^[4] as nucleophiles and little attention has been dedicated to the transformation of the less nucleophilic phenols,^[5] despite their strong industrial relevance. Phenols are important scaffolds found within the structure of several industrial intermediates such as bis-phenol-A and of several natural molecules. Furthermore, one of the most abundant biopolymers, lignin, features a polyphenolic structure that arises from the polymerization of *p*-coumaryl, coniferyl and sinapyl alcohols.^[6] The classical syntheses of esters from phenols involves activated acylating reagents such as acyl chlorides or anhydrides, while the direct esterification of a phenol with a carboxylic acid is known to be more difficult than with an aliphatic alcohol.^[7] In this context, harnessing catalytic carbonylation reactions as a versatile, atom-efficient and high-yielding entry into phenolic esters would be most attractive,

especially when allowing conversion of a broad scope of phenols. This prompted us to focus our attention on the synthesis of aryl and aryl nona-3,8-dienoates from the carbonylative coupling reaction of 2 equivalents of 1,3-butadiene followed by the nucleophilic attack of an alcohol (Scheme 1). This carbonylative version of the much more described telomerization reaction^[8] is highly atom-economical and involves reactants that are industrially accessible (butadiene, CO, alcohols). Moreover, the butadiene coupling reactions advantageously lead to the formation of two unsaturations and thus open the way to further functionalization. While this transformation has been only studied with aliphatic alcohols in seminal works by Tsuji, Billups and Knifton,^[9] it was only recently used in an intermediate step for the synthesis of α,ω -C10-diester.^[10] To the best of our knowledge, the reaction with phenols as (weak) nucleophile is still a challenge and we now wish to describe here such transformation with variously substituted phenols, natural phenols and a polyphenolic biopolymer such as Kraft lignin.



Scheme 1: The reaction of carbonylative telomerization reaction with phenols.

Results and Discussion

Initial studies were performed with *o*-methoxyphenol as model substrate, under reactions conditions close to those used by Tsuji for the catalytic transformation of aliphatic alcohols (Table 1).^[9b] The reaction was run in THF at 90°C under 20 bar of CO for 20 hours, with *in situ* generation of catalyst from a combination of 0.5 mol% Pd(OAc)₂ with 12 equivalents of PPh₃ (molar equivalent vs. palladium). Such reactions conditions were

[a] Mr C. Dumont, Dr. R. Gauvin, Pr. M. Sauthier.
Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France.

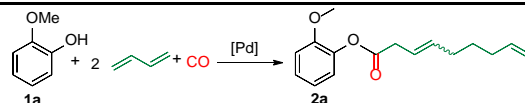
E-mail: mathieu.sauthier@univ-lille1.fr

[b] Mr C. Dumont, Dr. F. Belva.
ICAM site de Lille, 6 rue Auber, 59016 Lille Cedex, France.

Supporting information for this article is given via a link at the end of the document.

disappointing, only affording poor yield into the targeted esters.^[11] Attempts at improving the reaction outcome by tuning of temperature or CO pressure were not rewarding. The use of a base such as triethylamine did not lead to any improvement (See SI). A breakthrough was achieved with the use of benzoic acid as an additive in catalytic amount (compare entries 1 and 2 from Table 1). With 15 mol% of benzoic acid, the yield in ester reached 62 % and further increase of the loading of acid to 15 % and 30 % lead to respectively 88% and 98 % yield (entries 2-4).

Table 1. Carbonylative telomerization with *o*-methoxyphenol : Optimisation of catalytic reaction conditions.^{a)}

						
Entry	Pd(OAc) ₂ %	Acid %	T °C	PPh ₃ Eq/Pd	Butadiene Eq/OH	Yield (%) ^{b)}
1	0.5 %	0	90	12	7	6
2	0.5 %	8	90	12	7	62
3	0.5 %	15	90	12	7	88
4	0.5 %	30	90	12	7	98
5	0.5 %	30	100	12	7	95
6	0.5 %	30	80	12	7	25
7	0.5 %	30	70	12	7	10
8	0.5 %	15	90	8	7	99
9	0.5 %	15	90	6	7	90
10	0.5 %	15	90	4	7	88
11	0.5 %	15	90	2	7	23
12	0.5 %	15	90	4	6	85
13	0.5 %	15	90	4	4	87
14	0.5 %	15	90	4	2	49
15	0.5 %	30	120	12	7	85
16	0.25 %	30	120	12	7	90
17	0.1 %	30	120	12	7	49

a) Conditions : 9 mmol guaiacol, 10 mL THF, 20 bar CO, 22 h; % of benzoic acid, based on the amount of phenol b) determined by ¹H NMR, the conversions of phenols are identical to yields.

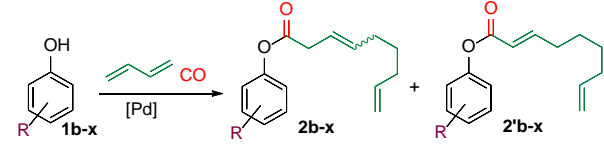
Rather similar yield was obtained at higher reaction temperature (entry 5, 100 °C) but lowering from 90°C to 80°C or 70 °C led to drastically decreased yield (entries 6 and 7). At these temperatures, higher catalyst loadings are needed to reach completion within 20 hours. The impact of the number of equivalents of phosphine with respect to palladium has been studied. At 90 °C with 15 mol% of benzoic acid, a quantitative



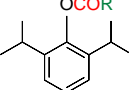
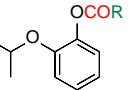
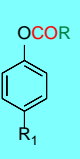
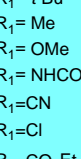
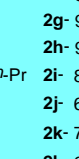
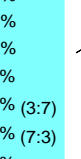
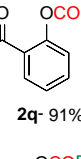
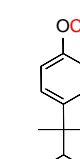

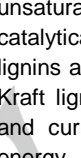



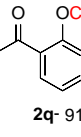
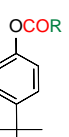
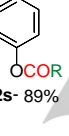
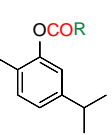
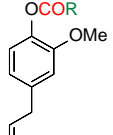
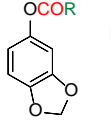
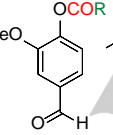
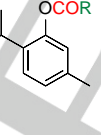
yield is obtained with 8 equivalents of phosphine. Excess of ligand is classically used to stabilize the low valent intermediates in solution (entries 8-10) : Below 4 equivalents, palladium black is observed at the end of the reaction, while affording only poor yield (entry 11). As exemplified in Table 1, an excess of butadiene is needed to reach high phenol conversion (entries 12-13). The use of a stoichiometric amount of 1,3-butadiene (2 equivalents / *o*-methoxyphenol) lead to a much lower yield (entry 14): At 90 °C, part of the butadiene is converted into side-products discarded using the classical work-up procedure, but which could be identified as oligomers after proper post-reaction treatment (See Scheme SI). With optimized reaction conditions at hand, catalytic loading was decreased to 0.25 % without detrimental effect on yield (entries 16 and 15), but further lowering the Pd charge to 0.1 % was not met with success (compare entries 15 and 17).

The scope of the reaction was explored with variously substituted phenols (Table 2). As a large number of synthetic or natural phenols are commercially available, we intended to both delineate the impact of the aromatic system substitution pattern on the yield of reaction and to apply our procedure to the synthesis of phenol esters using industrially relevant reactants. As expected, the less sterically hindered phenol **1b** was efficiently converted with 96 % isolated yield into the corresponding bisunsaturated ester **2b**. Despite the higher steric demand, derivatives **1c-e** were also quantitatively converted in the corresponding esters **2c-e**. Along this line, phenols *p*-substituted with electron donating groups such as *t*-butyl, methyl, methoxy or *N*-amido **1f-i** gave similar results to phenol **1a** with the corresponding esters obtained in high yield. Electron withdrawing groups in the *para*-position of the phenol lead to the formation of a mixture of two isomers **2j-l** and **2'j-l** albeit in lower yield while *p*-nitrophenol **1m** didn't show any reactivity. The exact structure of the isomers was determined from the reaction with **1k** that bears a cyano substituent on the *para* position of the phenol moiety. As shown by GC analysis of the crude, these isomers are obtained in a 1/1 ratio. A preparative TLC allowed the isolation of isomers **2j** (Z/E mixture) and **2'j**. ¹H and ¹³C NMR and HR-MS studies revealed the isomerization of the double bond from the allylic position to the conjugated position. Such isomerization from a β,γ- to an α, β-position is known to be promoted by bases.^[12-14] In the present case, under acidic conditions, the Pd-based catalytic system can lead to the formation of a palladium hydride, a species able to isomerize the double bond.^[15] The ratio of the two isomers obtained after 22 h of reaction is strongly dependent on the nature of the electron withdrawing group. Phenols with chloride and carboxyethyl groups in the *para*- positions lead to the formation of the esters **2k/2'k** and **2l/2'l** with, respectively, 3/7 and 7/3 ratios. A similar trend was observed with substituents on the meta-position of the phenol. **2n** was obtained as sole isomer from *m*-methoxyphenol while the presence of electron-withdrawing groups lead to the formation of **2o/2'o** and **2p/2'p** with respectively 3/2 and 1/1 ratios. These examples evidence a wide compatibility of the catalyst with the presence of several functionalities on *para* and *meta* positions. The tolerance to the presence of functions with a carbonyl group such as ketones was further assessed from the

transformation of *o*-acetylphenol in ester **2q** with 91 % yield. In addition, diphenols such as 1,4-dihydroquinone **1r** and bisphenol-A **1s** could also be efficiently converted in high yield, showing that tetra-unsaturated esters can be readily accessible from industrially relevant difunctionalized compounds.

Table 2. Scope of the reaction.^{a, b}



 2b- 96%	 2c- 99%	 2d- 99%	 2e- 99%
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>  2f- 84%  2g- 98%  2h- 99%  2i- 86%  2j- 63% (3:7)  2k- 77% (7:3)  2l- 68% (1:1)  2m- 0% </p> </div> <div style="width: 45%;"> <p>  2n- 99%  2o- 92% (3:2)  2p- 20% (1:1) </p> </div> </div>			
<div style="display: flex; justify-content: space-around;"> <div>  2q- 91% </div> <div>  2r- 83% (9:1) </div> </div>			
<div style="display: flex; justify-content: space-around;"> <div>  2s- 89% </div> </div>			
<div style="display: flex; justify-content: space-around;"> <div>  2t- 91% Carvacrol </div> <div>  2u- 99% Eugenol </div> <div>  2v- 95% Sesamol </div> <div>  2w- 85% Vaniline </div> <div>  2x- 98% Thymol </div> </div>			

a) Conditions: 9 mmol of phenol, 10 mL THF, 1% Pd(OAc)₂, 12 eq. PPh₃/Pd, 7eq. butadiene/ phenol, 0.15 eq. benzoic acid, 20 bar CO, 90 °C, 22h. b) The ratio β,γ-unsaturated ester / α,β-unsaturated ester is given under parenthesis.

As the phenol moiety is met in several natural compounds, several of such substrates were probed as substrates.

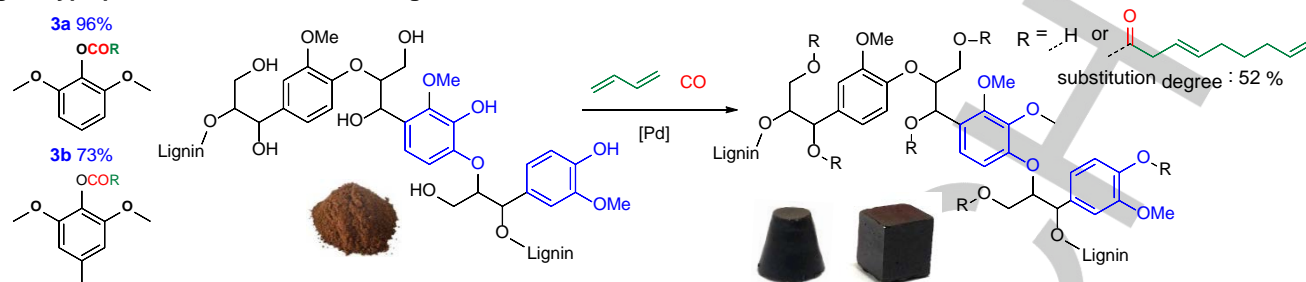
Carvacrol, eugenol, sesamol, vaniline and thymol afforded the expected esters **2t-x** with almost quantitative yields (Table 2).

While this shows that the reaction is tolerant to the presence of aldehyde, alkene and acetal, this also emphasizes the efficiency of this approach as a tool for bioresources upgrading. As highlighted in the introduction, phenols are motifs present in lignins. The O-functionalization of lignin is targeted to chemically modify such material and introduce new functionalities.^[16] Esterification of phenols is a relevant strategy to chemically modify lignins and thus enhance and/or tune their properties. For instance, this can lead to higher solubilities of the material in organic solvents for further use and modification, or to more readily processable materials, even achieving thermoplastic behaviour.^[17]

The esterification is however typically performed with acyl chlorides or anhydrides.^[18] Clearly, these protocols are limited by the stoichiometric amounts of salt or acid obtained as side-products after the reaction. Alternative catalytic procedures are thus needed, particularly if introducing new (potentially reactive) unsaturations in the material. In our ongoing approach to catalytically functionalize this agromaterial,^[19] we targeted lignins as phenolic-type reactants. A particular focus was put on Kraft lignin^[20] that is industrially produced on very large scale and currently essentially valorized through the production of energy. The material contains a large number of phenolic (the predominating hydroxyl function) and aliphatic alcohols that can both act as nucleophile in carbonylative transformations. Before tackling the direct transformation of lignin, we investigated the transformation of methoxy-substituted "lignin-type" phenols that have been previously reacted in the case of the telomerization reaction.^[21] 2,6-methoxyphenol and 4-methyl-2,6-methoxyphenol were efficiently converted in the corresponding esters **3a-b** despite the steric hindrance arising from the presence of one or two methoxy groups on the *ortho* positions of the phenol (Scheme 2). The reaction was performed with industrial grade Kraft lignin that contains 5.8 mmol/g of hydroxyl groups per gram of material (2 mmol/g of aliphatic alcohols and 3.8 mmol/g of phenols). in THF with Pd(OAc)₂ / PPh₃ as catalytic system (0.6% eq./OH, PPh₃/ Pd = 5) at 80°C for 50 h (See Scheme 2). Interestingly, in the case of Kraft lignin carbonylative conversion, the benzoic acid could be omitted. This is likely due to the presence of acidic functions in the lignin itself, as evidenced by ³¹P NMR titration after derivatization. After reaction, the lignin was precipitated with pentane, dried under vacuum and analyzed by ¹H NMR (Figure 1).

lignin type phenols

Kraft lignin



Scheme 2. Pd-catalysed carbonylation with lignin-type phenols and Kraft lignin conditions : 0.8g of Industrial grade Kraft Lignin, 2.5 mL of butadiene, 10 mL of degassed THF, 0.6% Pd(OAc)₂ (based on the amount of OH group titrated in the lignin), PPh₃/Pd = 5, 80°C, 20 bar of CO, 50h; The given structure is a simplified scheme of Kraft lignin that contains both phenolic and aliphatic alcohols (See ESI for the characterization of the lignin used for this study).

The comparison of the ¹H NMR spectrum of the material obtained after reaction with those of **2a** and ethane-1,2-diyl bis(nona-3,8-dienoate) (independently prepared by carbonylative telomerization with ethyleneglycol) clearly evidences the grafting of the hydroxyl groups on both phenolic and aliphatic moieties. Indeed, signals at 3.1 ppm and 3.3 ppm indicate that both phenols and aliphatic alcohols have been involved in the reaction, while the presence of signals from 5.3 to 5.9 ppm and at 5.0 ppm accounts for the allylic and terminal unsaturations. IR spectroscopy evidences the formation of ester functions (ν_{CO} : 1738 cm⁻¹). The conversion of hydroxyls was monitored by derivatization and titration with ³¹P NMR in the presence of an internal standard: This revealed 66% and 45% conversion of aliphatic and phenolics OH moieties, respectively, which accounts for conversion of 52 % of lignin's total hydroxyl groups.

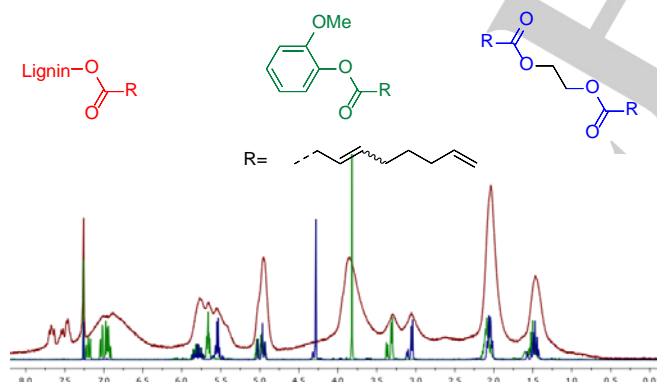
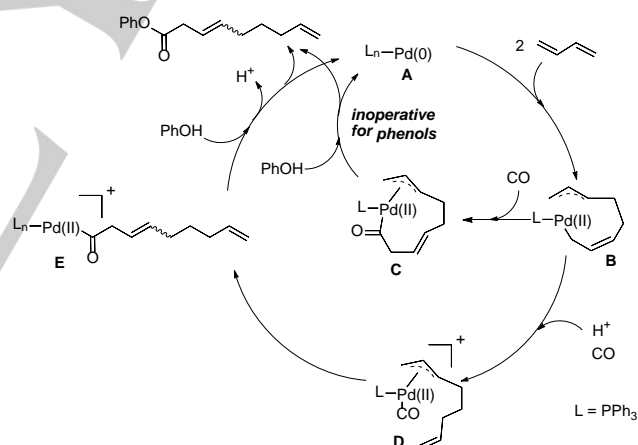


Figure 1. Comparison of the ¹H NMR spectra of the reacted lignin (red trace) with those of **3a** (green trace) and ethyleneglycol diester (blue trace).

This validates that using our optimized catalytic system affords efficient conversion not only of a broad scope of phenols, but also of a biopolymer for which controlled functionalization is of considerable interest. Moreover, rewardingly, the functionalized Kraft lignin could be moulded into objects of various shapes, as illustrated on Scheme 2, in contrast to the non-mouldable pristine material.

Recent insights concerning the mechanism of the telomerization reaction allow drawing a revisited version of the catalytic cycle proposed by Knifton for the carbonylative transformation.^[9c] The presence of the octadienyl moiety in the products obtained from both the telomerization and carbonylative telomerization reactions indicates that the corresponding catalytic cycles share the first oxidative coupling step (Scheme 3) that involves two equivalents of butadiene and the low valent Pd(0) species **A**. This step lead to the formation of an [(1- η^1 :6-8- η^3)-octa-2,6-diene-1,8-diyl]palladium(II) intermediate **B** stabilized with a PPh₃ ligand, as isolated and characterized by Beller,^[22b] or CO ligand.



Scheme 3. Proposed catalytic cycles of Pd-catalyzed carbonylative telomerization of phenols

As suggested by Knifton, a CO insertion step generates a neutral Pd(II) species **C** that ultimately leads to the formation of the ester product after reaction with an alcohol. In the case of a poor nucleophile such as phenol, this is not operative under non-acidic conditions. In agreement with the proposed catalytic cycle for the telomerization reaction,^[22] an alternative pathway may involve protonation of **B** that leads to the transient formation of a cationic monoallylic intermediate **D**. This step is clearly favoured in the present case by the presence of a catalytic amount of benzoic acid. In the following step, CO reacts with **C** to form a Pd-acyl species **E**. The cationic charge in **E** favours an attack by

soft nucleophile such as phenols that results in ester product formation, release of the acid and regeneration of **A**.

In conclusion, we have reported the palladium-catalyzed carbonylation of butadiene with phenols as nucleophiles. Benzoic acid used as co-catalyst has a key role in the efficiency of the reaction. This catalytic reaction opens a straightforward and high yield access to various aryl nona-3,8-dienoates from variously substituted phenols. Electron withdrawing groups on the *para* position of the phenol induce a partial isomerisation of the double bond. The protocol has been efficiently applied on the transformation of diphenols or phenols issuing from agro-resources. Furthermore, lignin-type phenols and industrial grade Kraft lignin were also efficiently converted. In the case of lignin, not only aliphatic alcohols but also phenolic moieties are grafted with nona-3,8-dienoate groups. This work shows that efficient, catalytic approaches based on the use of carbon monoxide to introduce carbonyl groups in the lignin can be designed and should find further developments.

Experimental Section

General Considerations

Kraft lignin was provided by UPM Biochemicals, Finland. Due to the high water uptake, neat kraft lignin was dried at reduced pressure at 60°C for 48h before use. Chemicals were purchased from Aldrich, Alfa Aesar, Acros and Strem. Butadiene was purchased from Linde Gas France and carbon monoxide from Air Liquide. Tetrahydrofuran was obtained from Acros and purified through a MBraun SPS-800 solvent purification system before use. The phenols were purchased from Sigma Aldrich and Acros.

DSC measurements were carried out using a Perkin-Elmer DSC 4000 differential scanning calorimeter. The measurements were done with a heating rate of 10 K/min in the temperature range from 243 K to 473 K, under nitrogen flow (20ml/min)

Diffuse reflectance infrared spectra were collected with a Harrick cell on a Nicolet Avatar spectrometer fitted with a MCT detector. Typically, 64 scans were accumulated for each spectrum (resolution of 4 cm⁻¹).

General procedure for the Carbonylative telomerisation of butadiene with Phenols – reaction with guaiacol.

Guaiacol (9 mmol), Pd(OAc)₂ (0,09 mmol, 20 mg), triphenylphosphine (0,53 mmol, 140 mg) and benzoic acid (1,4 mmol, 165 mg) were introduced into an autoclave and flushed under nitrogen. Degassed THF (10 mL) was added and the autoclave was cooled down to -40°C. Butadiene (28 mmol, 1,5 g, 2.5 mL) was condensed in a Schlenk tube cooled with an acetone/dry ice mixture and transferred through a cannula into the autoclave. The reactor was pressurized to 20 bar of CO, heated to 80°C and stirred with a magnetic stirrer overnight. After the reaction, the reactor was cooled to room temperature and the excess of gaseous butadiene was vented. The crude of

reaction was analyzed by GC and the pure product was obtained after silica gel column chromatography (99/1 Petroleum ether / Ethyl acetate – Yield 99%).

General procedure for the Carbonylative telomerisation of butadiene with Kraft lignin.

Lignin (800 mg), Pd(OAc)₂ (0,031 mmol, 7 mg) and the triphenylphosphine (0,16 mmol, 42 mg) were introduced into an autoclave and flushed under nitrogen. Degassed THF (10 mL) was added and the autoclave was cooled down to -40°C. Butadiene (28 mmol, 1,5 g, 2.5 mL) was condensed in a Schlenk tube cooled with an acetone/dry ice mixture and transferred through a cannula into the autoclave. The reaction was heated to 80°C and stirred with a magnetic stirrer overnight. After the reaction, the reactor was cooled to room temperature and the excess of gaseous butadiene was vented. The chemically modified lignin was precipitated with pentane (50 mL) and filtered. The resulting brown powder was dried at 60°C under reduced pressure for 24h (810 mg).

Acknowledgements

We are grateful to the Region Hauts-de-France and ICAM-Lille for C. Dumont's PhD fellowship. CNRS, Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur et de la Recherche, Région Hauts-de-France and FEDER are acknowledged for supporting and funding partially this work. We thank the company UPM Biochemicals for the generous loan of the Kraft lignin. We thank C. Delabre for the GC and GC-MS analysis.

Keywords: carbonylation • butadiene • phenol • lignin • palladium

- [1] a) L. Kollár *Modern Carbonylation Methods*; Wiley-VCH Verlag: Weinheim, 2008; b) M. Beller (editor), *Topics In Organometallic Chemistry*, Catalytic carbonylation reactions 2006, vol 18; c) M. Beller, A. M. Tafesh in *Applied Homogeneous Catalysis with Organometallic Compounds*, 2002, Wiley, Weinheim, vol 1, p 182; d) H.M.Colquhoun, D.J.Thompson, M.V.Twigg (editors) *Carbonylation, Direct Synthesis of Carbonyl Compounds* 1991, Plenum press, NewYork;
- [2] Fore reviews : a) P. H. Gehrtz, V. Hirschbeck, B. Ciszek, I. Fleischer *Synthesis* **2016**, 48, 1573-1596; b) X.-F. Wu, X. Fang, L. Wu, R. Jackstell, H. Neumann, M. Beller *Acc. Chem. Res.* **2014**, 47, 1041–1053; c) G. Kiss, *Chem. Rev.* **2001**, 3435; d) B. R. Sarkar, R. V. Chaudhari *Catalysis Surveys from Asia*, **2005**, 9, 193; e) W. Reppe, H. Kröper, *Liebigs Ann.Chem.* **1953**, 582, 38; f) M. Beltrani, C. Carfagna, B. Milani, R. Mancuso, B. Gabriele, F. Fini *Adv Synth & Catal* **2016**, 358, 3244-3253
- [3] Recent references for the synthesis of C5 esters : a) P.Neubert, M. Steffen, A. Behr *J. Mol. Catal. A: Chemical* **2015**, 407, 122–127; b) X. Fang, H. Li, R. Jackstell, M. Beller *Angew. Chem. Int. Ed.* **2014**, 53, 9030 –9034; c) A. Behr, L. Johnen, A. Wintzer, A. Willstumpf, M. Dingel *Catal. Sci. Technol.* **2013**, 3, 1573-1578; d) L. T. Mik, R. Tub, I. Tót, S. Pitte, I. T. Horváth *Organometallics* **2011**, 30, 4751–4764; e) M. Beller, A. Krotz, W. Baumann *Adv. Synth. Catal.* **2002**, 344, 517-524.
- [4] a) R. Pruvost, J. Boulanger, B. Leger, A. Ponchel, E. Monflier, M. Ibert, A. Mortreux, M. Sauthier *ChemSusChem* **2015**, 8, 2133-2137 ; b) R. Pruvost, J. Boulanger, B. Léger, A. Ponchel, E. Monflier, M. Ibert, A.

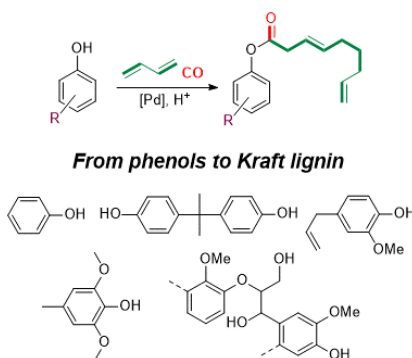
- Mortreux, T. Chenal, M. Sauthier *ChemSusChem* **2014**, 7, 3157–3163 ; c) A. Osichow, S. Mecking *Chem. Commun.* **2010**, 4980; d) S. B. Fergusson, H. Alper *J. Chem. Soc., Chem. Commun.* **1984**, 1349; e) D. Foster, H. Van Rensburg, R. P. Tooze WO 2008/023338 A1 and references herein; f) H. Isa, K. Karube, J. Nakayama US 4,244,882; 1981; g) Takeru Onoda, Keisuke Wada, Hironori Kageyama; Hideki Yamanouchi, Kenji Karube US 4,322,314; 1982; h) C. Shen, X. - F. Wu *Chem. Eur. J.* **2017**, 23, 2973; i) P. Kalck, M. Urrutigoity *Inorg. Chim. Acta* **2015**, 431, 110–121; j) S. T. Gadge, B. M. Bhanage *RSC Adv.* **2014**, 4, 10367–10389; k) X. F. Wu, H. Neumann, M. Beller *Chem. Rev.* **2013**, 113, 1–35; l) B. Gabriele, R. Mancuso, G. Salerno *Eur. J. Org. Chem.* **2012**, 6825–6839
- [5] Phenols have been for example used as nucleophile in the carbonylation of aryl halides and aryltriflates : a) X.-F. Wu, H. Neumann, M. Beller *ChemCatChem* **2010**, 2, 509–513; b) D. A. Watson, X. Fan, S. L. Buchwald, *J. Org. Chem.* **2008**, 73, 7096–7101; c) J. T. Joseph, A. M. Sajith, R. C. Ningegowda, S. Shashikanth *Adv. Synth. Catal.* **2017**, 359, 419;
- [6] G. Gellerstedt, G. Henriksson, in *Monomers Polym. Compos. Renew. Resour.* (Eds.: M.N. Belgacem, A. Gandini), Elsevier, Amsterdam, **2008**, pp. 201–224
- [7] For a difference of reactivity between aliphatic alcohol and phenol in esterification reaction through carbodiimide coupling : R. Shelkov, M. Nahmany, A. Melman *Org. Biomol. Chem.*, **2004**, 2, 397–401
- [8] a) N. Yoshimura in *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1 (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **2000**, p. 361; b) J. Tsuji, *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, Wiley, Chichester, 995, p. 422; c) J. M. Takacs in *Comprehensive Organometallic Chemistry II*, Vol. 12 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, **1995**, p. 785; d) R. F. Heck, *Palladium Reagents in Organic Syntheses*, Academic Press, London, 985; e) A. Behr, in *Aspects of Homogeneous Catalysis*, Vol. 5 (Ed.: R. Ugo), Reidel, Dordrecht, **1984**, p. 3; f) W. Keim, A. Behr, M. Röper, in *Comprehensive Organometallic Chemistry*, Vol. 8 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon Press, Oxford, **1982**, p. 372; g) A. Behr, M. Becker, T. Beckmann, L. Johnen, J. Leschinski, S. Reyher, *Angew. Chem. Int. Ed.* **2009**, 48, 3598–3614.
- [9] a) W. E. Billups, W. E. Walker, T. C. Shields, *Chem. Commun.* **1967**, 1067; b) J. Tsuji, Y. Mori, M. Hara *Tetrahedron* **1972**, 28, 3721–3725; c) J. F. Knifton *J. Catal.* **1979**, 60, 27–40
- [10] D. Vogelsang, B. A. Raumann, K. Hares, A. J. Vorholt *Chem. Eur. J.* **2018**, 24, 2264–2269
- [11] After purification by silica gel column chromatography, ¹H NMR analysis indicates the formation of a with a 20/80 ratio Z/E mixture of the esters
- [12] J. Tsuji, H. Yasuda, *J. Organomet. Chem.* **1977**, 131, 133–135
- [13] S. G. Alcock, J. E. Baldwin, R. Bohlmann, L. M. Harwood, J. I. Seeman *J. Org. Chem.* **1985**, 50, 3526–3535
- [14] F. Cros, B. Pelotier, O. Piva *Eur. J. Org. Chem.* **2010**, 5063–5070
- [15] a) A. L. Kocen, M. Brookhart, O. Daugulis *Chem. Commun.* **2017**, 53, 10010–10013; b) P. Mamone, M. F. Grünberg, A. Fromm, B. A. Khan, L. J. Gooßen *Org. Lett.* **2012**, 14, 3716–3719; c) X. Wang, L. K. Woo *J. Mol. Catal. A: Chemical* **1998**, 130, 171–176.
- [16] a) C. Wang, S. S. Kelley, R. A. Venditti, *ChemSusChem* **2016**, 9, 770–783; b) D. Kai, M. J. Tan, P. L. Chee, Y. K. Chua, Y. L. Yap, X. J. Loh, *Green Chem.* **2016**, 18, 1175–1200; c) S. Laurichesse, L. Averous, *Prog. Polym. Sci.* **2014**, 39, 1266–1290.
- [17] O. Gordobil, E. Robles, I. Egüés, J. Labidi, *RSC Adv.* **2016**, 6, 86909–86917
- [18] a) X. Zhao, Y. Zhang, L. Wei, H. Hu, Z. Huang, M. Yang, A. Huang, J. Wua, Z. Feng *RSC Adv.*, **2017**, 7, 52382; b) N. Cachet, S. Camy, B. Benjelloun-Mlayah, J.-S. Condoret, M. Delmas *Ind. Crops Prod.* **2014**, 58, 287–297; c) G.-H. Delmas, B. Benjelloun-Mlayah, Y. Le Bigot, M. Delmas, *J. Appl. Polym. Sci.* **2011**, 121, 491–501; d) W. Thielemans, P. R. Wool *Biomacromolecules* **2005**, 6, 1895–1905.
- [19] C. Dumont, F. Belva, R. M. Gauvin, M. Sauthier, *ChemSusChem*, **2018**, 11, 1649–1655.
- [20] G. Gellerstedt, *Ind. Crops Prod.* **2015**, 77, 845–854
- [21] P. J. C. Hausoul, S. D. Tefera, J. Blektoon, P. C. A. Bruijninx, R. J. M. Klein Gebbink, B. M. Weckhuysen *Catal. Sci. Technol.* **2013**, 3, 1215–1223
- [22] a) P. J. C. Hausoul, M. Lutz, J. T. B. H. Jastrzebski, P. C. A. Bruijninx, B. M. Weckhuysen, R. J. M. Klein Gebbink *Organometallics* **2013**, 32, 5047–5057; b) F. Vollmüller; J. Krause; S. Klein; W. Magerlein; M. Beller, *Eur. J. Inorg. Chem.* **2000**, 1825–1832; R. Benn, G. Schenker, K. P. Schick, G. Schroth, *Organometallics* **1985**, 4, 1945–1953; d) P. W. Jolly, R. Mynott, B. Raspe, K. P. Schick *Organometallics* **1986**, 5, 473–481.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

The efficient carbonylative conversion of two equivalents of butadiene with phenols into esters is promoted by palladium-based catalysts with benzoic acid as co-catalyst. Substrate scope encompasses variously substituted phenols, naturally-occurring phenols and industrial grade Kraft lignin.



C. Dumont, F. Belva, R. M. Gauvin, M. Sauthier*

Page No. – Page No.

The Palladium-Catalyzed Carbonylative Telomerization Reaction with Phenols, Polyphenols and Kraft Lignin