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Introduction

In recent years, metallic nanoparticles have been intensively developed as relevant catalytic systems.^{1–3} Owing to their high surface/volume ratio and potential recyclability, they are considered as the interface between homogeneous and heterogeneous catalyses.^{4,5} Moreover, they often combine improved activities and better selectivity which qualify them as more sustainable catalysts.⁶ Palladium nanoparticles (Pd-NPs) are among metallic nanoparticle catalysts, widely studied for industrially relevant reactions such as carbon–carbon cross coupling, reduction of nitroarenes, hydrogenation of alkenes and alkynes, and oxidation of primary alcohols.^{7–14} Usually the use of Pd-NPs in catalysis is performed through immobilization on a solid support^{14–17} which could impair their efficacy.

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"Water soluble" palladium nanoparticle engineering for C–C coupling, reduction and cyclization catalysis†

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The use of Pd nanoparticles (Pd-NPs) to realize several important organic reactions allows efficient catalysis with low metal loading (<1000 ppm), hence providing a greener catalytic system. However, to be truly green Pd-NPs need to be synthesized in a sustainable manner and be able to react in aqueous media in order to avoid the use of organic solvents. Here we describe an original and eco-friendly synthesis of Pd-NPs (using benign reactants and simple conditions) perfectly stable in water. Remarkably, this synthesis allows for control over their size and morphology by simply tuning the pH of the stabilizer. We then evaluate the catalytic efficiency of these Pd-NPs on six different model reactions (Suzuki Miyaura, Sonogashira, Heck, nitrophenol reduction and pentynoic cycloisomerization) in aqueous media. We show that the stabilizer structure influences the activity owing to its ability to promote the mass transfer of the organic substrates towards the NP surface in the aqueous environment. Finally, catalytic evaluations show that our nano-catalysts prepared in an eco-friendly manner are among the best catalysts described so far in the literature in each case, with high turnover frequencies reached with a low loading of palladium.

> More recently, the use of water as a benign solvent in biphasic systems have been attracting increasing interest to enhance the sustainability of the catalytic process.¹⁸ Nevertheless, two main challenges have to be overcome for the development of such a methodology: first, the direct synthesis of well-controlled Pd-NPs stabilized in water avoiding the tedious "ligand exchange approach"; second, the difficulty in allowing the mass transfer of organic substrates into the aqueous catalytic phase and therefore reaching high efficacy with low Pd loading. On the latter issue, the addition of amphiphilic compounds to the reaction media⁵ to promote the phase exchange has been successfully developed in the last decade by several groups.¹⁹⁻²⁴ While the results are promising, the NPs are the best catalysts not synthesized in a sustainable manner (high temperatures, organic solvents, dry argon, and expensive metal derivatives). Another option is the use of green bio-reductants,²⁵ which also act as stabilizers. This more economical and environmental solution appears nevertheless to yield less reactive catalysts²⁶⁻²⁹ and reproducibility could also be questioned owing to the high variability in the bio-extract composition. Alternatively, other authors proposed the use of ionic liquids, water-soluble NHC stabilizers, phosphine oxide polymers or other small organic stabilizers³⁰⁻³⁷ to stabilize the Pd-NPs in the aqueous media while allowing the mass transfer of the organic substrates. The latter approach is particularly attracting, as the strength and types of interactions between

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the stabilizer and the surface could be fine-tuned by an appropriate stabilizer design.^{38,39}

Herein, we report the straightforward and controlled synthesis of Pd-NPs perfectly stable in water and able to catalyse organic reactions in aqueous media. Our approach is based on an eco-friendly synthesis using benign conditions: the use of sodium ascorbate as a bio-reductant conjugated to bio-compatible phosphonic acid stabilizers. To the best of our knowledge phosphonic acids have never been used for Pd-NP synthesis. These molecules present several important advantages as NP stabilizers compared to other small molecules and green bioreductants. First, they present a unique multidentate robust and stable binding to the metallic surface and therefore have emerged since three decades as important tools for the preparation of organic-inorganic nanomaterials with important and various applications.^{40,41} They have been used for corrosion inhibition purposes, to produce a rich variety of hybrid metalorganic frameworks, to control interfacial properties in organic-electronic devices and photovoltaic cells, to modify implanted biomaterials, to produce biosensors, etc. Second, they can benefit from a great variety of chemical structures with relatively low toxicity (compared for example to phosphine). The preparation of phosphonates is long known and well described and has allowed the production for over a century of numerous commercial structures readily available and studied,42 with some molecules being also used as therapeutic agents.43 Hence, the second asset permits a perfect tuning of the structure of these stabilizers which could allow for creating a lipophilic environment at the surface, enhancing the mass transfer of organic substrates. The methodology we describe using phosphonic acids as stabilizers ensures the production of highly stable and dispersible Pd-NPs in aqueous media. Then, the great versatility of these nanocatalysts was reported. We evaluated the same catalyst on an unprecedented number and types of reactions: 6 different important reactions (C-C coupling, reduction and cyclization) in an aqueous medium without any additives (amphiphilic compounds, supplementary ligands, and other metals) and with extreme efficiency compared to previous solutions, reaching ppm loading of Pd and high turnover frequencies (TOFs).

Results and discussion

Choice of ligand for the synthesis of Pd NPs

Phosphonic acids and more precisely the hydroxyl methylene bisphosphonic acid family that are molecules long known for their chelating properties towards metal ions were chosen as stabilizers to perform our synthesis. They were industrially used during the XXth century as water softeners. Following the work of Fleish in 1960 they have been then studied for their numerous therapeutic properties towards diverse pathologies (osteoporosis, cancer, and anti-trypanosoma).^{44,45} Some of these compounds are actually commercialized as common treatment of osteoporosis. More recently they have been utilized for the coating and functionalization of various metal

oxide NPs⁴⁶⁻⁵¹ and shown to have the ability to not only stabilize metallic NPs (gold or silver) but also allow for their synthesis by reduction of metal salts.⁵²⁻⁵⁷ It was hypothesized that the molecules will allow for a moderate coordination to the surface (better than carboxylate but weaker than common Pd stabilizers such as phosphine, thiol or amine) not impairing catalysis. Additionally, they will permit a good stabilization in aqueous media as already described for other types of NPs. Among this family of compounds, several molecules listed in Scheme 1 were chosen for this study. Compound 1 presenting an alkene functionality was used for comparison with precedent work on gold NPs.^{53,54} Compound 2 was chosen as an example of a known FDA approved and commercialized molecule (FOSAMAX®) already studied by Benyettou et al. for silver NP synthesis.⁵⁵ Compounds 3 and 4 were chosen as they present aromatic functionalities that could in our opinion allow for better reactivity of organic substrates, mostly aromatic, at the surface of the Pd-NPs. Compound 5 was chosen as it is a simple structure that is produced on a large scale and used in industry since a long time. Finally, our protocol was also evaluated with a more simple structure of commercial phosphonic acid (benzyl phosphonic acid 6) and with a commercially available polymer bearing acid phosphonic functionality 7 already used for the coating of iron oxide NPs (PEOMA co MAPC1 ACID).58,59

We perform NP synthesis in water under aerobic conditions as all the molecules 1-3 and 5-7 are readily soluble in water besides pH = 3. Only compound 4 is soluble besides pH = 9.

Synthesis and characterization of Pd NPs

In the first approach, based on our precedent experience in gold NP synthesis, we evaluated the synthesis protocol without addition of any supplementary reductant. Unlikely to what was observed with gold the bisphosphonic function was not sufficient a reductant to allow the formation of Pd-NPs even under prolonged heating conditions. Therefore, a supplemen-



Scheme 1 Phosphorus stabilizers evaluated for the synthesis of Pd-NPs.

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tary reductant was added to trigger the nucleation. Sodium ascorbate was chosen because it is environmentally friendly and biocompatible. This reducing agent has already been used to synthesize Au-NPs^{52,60} or Pd-NPs.^{61,62} Typically, reactions are performed by mixing a stock solution of Na₂PdCl₄, the phosphorous stabilizer in water at three different pH values (3, 7, and 10) and sodium ascorbate. The mixture is then heated in a microwave reactor for 30 min at 100 °C. The reaction is run under complete aerobic conditions. Apparition of a brown to dark brown colour visually assesses the formation of Pd-NPs. By running UV-vis the complete disappearance of the band centred at 430 nm characteristic of PdCl₄²⁻ in water could be verified (see the ESI[†]). One must note that Pd-NPs obtained from the acidic solution (pH = 3) of compound 3 (noted Pd-NP-3A) present a non-negligible absorbance at a wavelength higher than 700 nm compared to Pd-NPs obtained from the basic solution (pH = 10) of compound 3 (noted Pd-NP-3B) (see the ESI[†]).

The formation of the Pd-NPs was observed whatever the phosphorus compound used. When realizing the synthesis without any phosphorus stabilizer the discoloration of the Pd (II) solution was immediate without the need for heating but the grey solution produced quickly led to the formation of a black precipitate. The replacement of the sodium ascorbate by a solution of sodium borohydride reacted in the presence of phosphorus stabilizers led also instantly to the formation of a black solution that precipitates rapidly. Only when treated with the phosphorus stabilizer and sodium ascorbate does the solution stay highly stable during time and do not evolve over time (no colour modification and no precipitation). The variation of the pH of the stabilizer solution was studied (pH was set at 3, 7 and 10). For most of the compounds studied when realizing the synthesis with solution at acidic pH, the discoloration of the reaction media was quicker and, in some cases, Pd-NPs were formed at room temperature. For solution at pH = 7 or 10 discoloration was only observed when heating the solution for 30 min. The transmission electronic microscopy analysis of the produced Pd-NPs was realized for each reaction condition. Whatever the phosphorus stabilizer used the morphology of the Pd-NPs formed was very similar and depends essentially on the pH of the starting stabilizer solution (Fig. 1 and 2). The basic solutions of the phosphorus stabilizer yield small Pd-NPs <10 nm (from 2 nm to 7 nm depending on the stabilizer) and monodisperse (Fig. 1).

On the other hand, the acidic or neutral solutions of the stabilizer yield un-homogeneous population of Pd-NPs with the formation of larger NPs >50 nm and small NPs (<5 nm) in the background. In the case of a stabilizer bearing aromatic side chains (compounds **3**, **4** and **6**) a particular phenomenon was observed when reacting under the acidic solutions. The larger particles formed were constituted in a homogeneous manner of spherical agglomeration of small Pd-NPs in the form of nanodendrites or nanorasberries (Fig. 2). The formation of these anisotropic forms of Pd-NPs can explain the absorption differences noted on UV spectra (see the ESI†). These nanodendrites or nanorasberries were usually better



Fig. 1 TEM micrograph of Pd-NPs obtained with basic solutions of compound 1: Pd-NP-B1 (A and B), compound 4: Pd-NP-B4 (C and D) and compound 2: Pd-NP-B2 (E and F).



Fig. 2 TEM micrograph of Pd-NPs obtained with acidic solutions of compound **3**: Pd-NP-A**3** (A and B) and compound **6**: Pd-NP-A**6** (C and D).

defined when performing heating without microwave. Moreover, they could be separated from the small NPs in the background by simply concentrating and washing the solution over 100 kDa membranes using centrifugation. This difference in shape observed for the produced NPs may be due to the difference in the pH of the phosphonic acid stabilizer and



ig. 3 HRTEM micrograph of Pd-NP-B3 (inset: SAED pattern).



Fig. 5 Typical (A, B) P 2p and Pd 3d peaks recorded on (A) compound 3 powder and (B, C) Pd-NP-B3.

therefore could be due to differences in stabilizer complexing properties allowing for differences in the growth mechanism of the NPs.⁶³

Further morphological and crystallographic features of Pd NPs obtained with the basic solution of 3 (Pd-NP-B3) were studied by HR-TEM. Pd-NP-B3 exhibits spherical NPs of around 6 nm (Fig. 3). The SAED pattern shows clearly the presence of the crystal phase through the appearance of (111), (200), (220) and (311) diffraction planes of the cubic closest packed structure of palladium. The inter-reticular distance was assessed using the intensity line profiles revealing lattice planes distancing by $d_{111} = 2.25$ Å as indicated in the HRTEM micrograph.

All the Pd-NPs were purified by dialysis to remove the unbound phosphonic stabilizer and lyophilized prior to FTIR and XPS analyses. The FTIR spectrum of Pd-NP-B3 clearly shows the vibration bands associated with the phosphonic moiety bound at the surface of a metal (Fig. 4). Indeed, as already described on several NP surfaces (iron oxide, gold or silver)^{48,54,55} a merging of the sharp absorption bands consist-



Fig. 4 FTIR spectra of the $500-2000 \text{ cm}^{-1}$ area for Pd-NP-B3 (in blue) and free compound 3 (in black).

ent with phosphonic acid present in the 850–1300 cm⁻¹ fingerprint (ν P=O at 1162, 1109 and 1062 cm⁻¹; ν_s , ν_{as} of PO₃ at 1035, 997 and 965 cm⁻¹; and ν POH at 899 cm⁻¹) is observed to yield one broad band centred around 1090 cm⁻¹ (Fig. 5).

P 2p peaks recorded on Pd-NP-B3 and on powder of 3 are shown in Fig. 5. P 2p consists of a doublet due to the spinorbit coupling, P $2p_{3/2}$ and P $2p_{1/2}$, separated by 0.9 eV and a ratio of 2:1 between their areas.⁶⁴ This yields a full width at half maximum (FWHM) equal to 1.5 ± 0.1 eV in all situations. The P 2p peak shows a poor signal-to-noise ratio on Pd-NP-B3 compared to 3 powder, owing to the low amount deposited on the flat substrate. The binding energy value of the P $2p_{3/2}$ component was 134.0 eV on 3 powder (Fig. 5A) and shifted to lower binding energies, about 132.5 eV, on Pd-NP-B3 (Fig. 5B). This significant shift ($\Delta_{BE} \sim 1.4$ eV) suggests the coordination of the phosphate head group to the metal, as observed on other phosphate-metal/oxide interfaces.^{65,66} The Pd 3d peak, including Pd 3d_{5/2} and Pd 3d_{3/2} doublets, is presented in Fig. 5C. It shows a main contribution at 335.6 eV due to Pd(0). The distance between Pd 3d_{5/2} and Pd 3d_{3/2} peaks of the Pd 3d doublet was fixed at 5.25 eV,⁶⁷ and a ratio of 0.6 was imposed between their areas. The peak also includes lower contributions at higher binding energies. A component at ~336.9 eV is attributed to the PdO compound, indicating a possible oxidation of Pd-NPs. The component at 338.0 eV is also attributed to Pd oxide, PdO₂, but may include a contribution due to the PdCl₄²⁻ compound,^{67,68} probably originating from the traces of the unreacted precursor.

The average number of phosphonic molecules per Pd-NP was deduced by electron dispersive X-ray (EDX) analysis on which the presence of phosphorus and palladium is clearly visible (Fig. 6). For example, for Pd-NP-B3 (average diameter, 6 nm) an average number of 270 (\pm 50) molecules per Pd-NP was deduced. This represents a surface area of approximately 0.4 nm² occupied by the bisphosphonic function. This value is in accordance with the previous results obtained for iron oxide or gold NPs.

 ζ potential analyses were also performed to measure the surface potential of Pd-NPs covered by phosphonic acids. As expected at pH = 7 the ζ -potential is clearly negative from -40

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Fig. 6 EDX analysis of Pd-NP-B3.

to -30 mV in accordance with the presence of the phosphonate function at pH = 7 at the surface of the NPs.

Nano-catalyst evaluation

The catalytic abilities of the obtained Pd-NPs were evaluated on three different C–C cross-coupling reactions (Suzuki-Miyaura, Sonogashira and Mizoroki-Heck reactions), on two reduction reactions chosen as model reactions (the reduction of 4-nitrophenol^{10,69} and the reduction of styrene)^{30,34,70,71} and finally on a cyclization reaction (the pentynoic acid cycloisomerization)⁷² (Scheme 2).



Scheme 2 Reactions catalysed by Pd-NPs: from top to bottom: Suzuki–Miyaura, Sonogashira, Mizoroki-Heck (with styrene or methyl acrylate) and 4-nitrophenol reduction.

The three cross coupling reactions are by far the most popular C-C coupling processes often used to describe the catalytic potency of new catalysts.⁵ These reactions are still highly studied as they have many desirable features for largescale synthesis and are amenable for the industrial synthesis of pharmaceuticals and fine chemicals. On the other hand, nitroarenes are significantly toxic by-products produced from pesticides, herbicides and synthetic dyes and therefore their removal from the environment is of high importance. The reduction of 4-nitrophenol is considered as a model reaction to evaluate the potency of NP catalysts. The cycloisomerization of pentynoic acid to the corresponding alkylidene lactones was chosen as a model reaction of cyclo-isomerization involving alkyne substrates, as it is a general process that is known to permit an atom-economical preparation of several hetero-aromatic rings.

C-C coupling reactions. All the C-C coupling reactions were evaluated under similar conditions with different Pd-NPs (differing by the stabilizer used and the shape of the NPs formed). For these reactions, 4-halogenonitrobenzene was chosen as the substrate. The reaction was run in a mixture of water/ethanol (1/1) in the presence of potassium carbonate as a cheap base corresponding to green chemistry principles and by heating the mixture in a microwave reactor at 80 °C. Conversions were estimated by Gas Chromatography (GC). Products were purified by column chromatography and characterized by ¹H and ¹³C NMR (see the ESI[†]). Globally all the Pd-NP catalysts were able to perform the catalysis, and the best results were always obtained with Pd-NPs of small size produced from the reaction with stabilizers at basic pH (nanoraspberries were less reactive for C-C coupling reactions). The results were similar when varying the phosphorous stabilizer (differences will be discussed further on) and the best results were obtained with Pd-NPs obtained with stabilizers 3, 4 and 6 and we mainly focused our study on Pd-NP-B3.

The Suzuki-Miyaura reactions were performed by condensing 4-halogenonitrobenzene with 4-tolyl boronic acid in the presence of sodium carbonate. From the iodide derivative, complete conversion was obtained in 30 min by heating to 80 °C. The catalyst loading could be decreased down to 0.002 mol% in palladium which represents a quantity of palladium (in mole) with respect to the substrate of 20 ppm. With 10 ppm of palladium the conversion is still 80%. When using the less expensive bromide substrate the conversion was complete keeping the same conditions with a Pd loading of 0.01 mol%. Under all these conditions, no secondary products (dehalogenation or homocoupling) were detectable on the ¹H NMR spectra of the crude mixture, and only the desired product was formed. It should be pointed out that when conversion was complete no purification was needed as after organic extraction the only compound isolated was the product of Suzuki coupling. With the chloride substrate with 0.1 mol% of Pd loading no conversion was observed. Only when the reaction time was increased to 120 min traces of the product were obtained (conversion <20%). Turnover frequencies (considering the surface Pd atom TOF_{surf}) were calculated

(at conversion <50%) and the results correspond for iodide and bromide to the TOF_{surf} values of 130 020 and 91 320 h⁻¹ respectively. When working at 0.01 mol% of Pd (100 ppm) using the iodide derivatives the catalyst can be recycled at least three times without any decrease in conversion. The recycling was simply performed by extracting the product from the aqueous medium and reintroducing the reactants in the solution for the following reaction. Recycled Pd-NPs were evaluated by TEM (see the ESI†). While extremely low quantity of NPs could be found on the TEM grid due to the ppm amount of Pd used, they did not appear to have been modified during the synthesis. Unfortunately, such a small amount of material could not allow performing XPS analysis to characterize their surface and potential modification in the Pd state.

For the Sonogashira reaction, we conducted the reaction of phenylacetylene with 4-halogenonitrobenzene. It is important to note that the reactions were performed in the absence of any additives usually utilized such as copper or phosphine ligands. For the iodide derivative, the conversion was 97% after 30 min at 0.015 mol% in Pd (150 ppm), and for the bromide derivative the conversion was complete after 3 h at 0.2 mol% in Pd. The TOF_{surf} (calculated at conversion <50%) corresponds for the iodide and bromide derivatives to 46 440 and 180 h⁻¹ respectively. For the chloride derivative under the same conditions as the bromide conversion higher than 20% was never reached, even by increasing the reaction time up to 24 h.

For the Mizoroki-Heck reaction two different substrates were evaluated on 4-iodonitrobenzene: ethyl acrylate and styrene. For the reaction with acrylate complete conversion was observed at 0.1 mol% in 2 h, and a TOF_{surf} of 1200 h⁻¹ was calculated. For the less reactive styrene the conversion was only 70% at 0.2 mol% in 3 h.

Influence of the stabilizer on catalytic activity. When evaluating Pd-NPs bound to any solid support, the activity is dependent upon the structure and the interactions of the stabilizers at the surface because they control the accessibility of the substrates³¹ and it is especially important during the reaction of organic substrates in an aqueous environment. In order to evaluate the effect of the stabilizers on the catalysis efficiency, we compared the activity of Pd-NPs obtained from compounds 3, 5 and 7 at basic pH (Pd-NP-B3, Pd-NP-B5, and Pd-NP-B7) on the Suzuki coupling of 4-bromonitrobenzene with 4-tolylboronic acid. These stabilizers led to similar particle size and therefore the nanocatalysts only differ from the stabilizer constitution. Using strictly identical conditions (reaction for 30 min at 80 °C in the water/ethanol mixture), the best results were observed using Pd-NP-B3 that bears a benzyl functionality (80% conversion using 0.001 mol% of Pd). The conversion was slightly decreased with Pd-NP-B5 bearing a methyl group in place of a benzyl group (60% conversion using 0.001 mol% of Pd), whereas Pd-NP-B7 was far less active (only 40% conversion using 0.01 mol% of Pd). This result clearly indicates that the constitution of the stabilizer is determinant on the catalyst activity in aqueous media. As we hypothesized, the Pd-NPs bearing aromatic functionalities led to more active catalysts.

The stabilizer probably allows for improving the substrate concentration close to the surface. On the other hand, when using a polymer coating that permits more effective steric stabilization, the catalysis efficiency is impaired. The latter difference could be attributed to the decrease in the accessibility of the substrate in the case of a macromolecular stabilizer.

Mechanism considerations. During the last few years there have been important debates on the nature of catalytic species involved when using Pd-NPs for cross coupling reactions.¹⁴ The question being: does the active catalyst is the Pd-NPs or leached soluble palladium species in the reaction medium? Such leaching of Pd species is usually described to happen in the case of prolonged heating and is described to be due to the oxidative addition of aryl iodide or bromide.¹⁴ Another possible source of Pd leaching species could come from the redissolution of amorphous PdO on the surface (the presence of such species was evidenced by XPS). In our case, though it cannot be totally ruled out, the mild conditions and the short reaction time pledge for a reaction at the surface of the NPs rather than through the dissolution of Pd species. Due to the high stability of the Pd-NP colloids in the media, the "hot filtration test" was impossible to further identify the active species. However, when studying Pd-NPs after several reactions they still appear spherical in shape with the same size (see the ESI[†]). Unfortunately, owing to the low quantity of Pd-NPs used, XPS analysis could not be performed to further analyse them. Moreover, it is generally described that when leaching arises through the oxidative addition of aryl halide a dehalogenation product is formed.¹⁴ In our case, no such by-product was observed even when the reaction time and temperature were increased.

Comparison with similar catalysts. When compared to the literature (Table 1) it appears that the results of Suzuki-Miyaura, Sonogashira and Heck C-C coupling obtained for our Pd-NPs are equivalent to what was described for several other "water soluble" (unsupported or supported) Pd-NPs whatever the preparation mode and performed under similar conditions. Compared to the closest solution consisting of water soluble phosphine ligands the phosphonic acid coated Pd-NPs present a clear advantage in terms of catalytic efficiency.^{32,34} Moreover, our results are even in the same range as the best "homeopathic palladium nanoparticle" water soluble catalysts described in the literature so far^{21,73} (Table 1). Finally compared to some of the best solutions described in the literature¹⁴ our phosphonic acid coated Pd-NPs still appear competitive and in the range of the best catalysts reported so far for Suzuki–Miyaura⁷⁴ and Sonogashira.⁷⁵ Concerning the Sonogashira reaction, one must note that comparable Pd based nanocatalysts are often processed with organic solvents (except for the supported solution presented in ref. 75) in contrast to our catalyst reaching high efficiency in the water/ ethanol mixture.

Reduction of nitrophenol. The reduction of 4-nitrophenol with Pd-NP-B3 as a catalyst was evaluated in water at room temperature with an excess of sodium borohydride and the evolution of the reaction was followed by assessing the dis-

Catalyst	Reaction type	Conditions	mol% Pd forcomplete conversion	TOF (h^{-1})	Ref.
Pd-NP-B3	SM	H ₂ O/EtOH (1:1), K ₂ CO ₃ , 80 °C, 30 min	0.002 (iodide)	130 020	This work
Pd-NP-B3	S	H ₂ O/EtOH (1 : 1), K ₂ CO ₃ , 80 °C, 30 min (iodide) 3 h (bromide)	0.015 (iodide) 0.2 (bromide)	91 320 46 440 180	This work
Pd-NP-B3	Н	H ₂ O/EtOH (1:1), K ₂ CO ₃ , 80 °C, 2 h	0.1 (iodide)	1200	This work
CB[6]-Pd NPs	SM	H ₂ O/EtOH (1:1), Na ₂ CO ₃ , 40 °C, 20 min	0.5 (iodide)	N.D.	76
Pd/MFC	SM	EtOH, K_2CO_3 , reflux, 1 h	0.3 (iodide)	16.67	77
Pd/MFC	Н	DMF, K ₂ CO ₃ , 120 °C, 1 h	0.3 (iodide)	16.5	77
Fe-ppm Pd catalysis	SM	H ₂ O, 2 wt% TPGS-750-M, S-Phos (5 mol%) K ₃ PO ₄ , 45 °C, 11 h	0.032 (bromide)	N.D.	21
Dendrimer PdNPs	SM	H ₂ O/EtOH, K ₃ PO ₄ , 80 °C, 1.5 h	0.001 (bromide)	39 600	73
MEPI-Pd	SM	H ₂ O (TBAF), K ₂ CO ₃ , 100 °C, 30 h	0.000028 (iodide)	119 000	74
Branched Pd NCs	SM	H ₂ O/EtOH (1:3), K ₂ CO ₃ , 50 °C	0.5	1364	78
Pd NPs with a PEG-tagged stabilizer	SM	H ₂ O, K ₃ PO ₄ , 90 °C, 1 h	0.25	N.D.	35
TPPTS capped Pd NPs	SM	H ₂ O, K ₃ PO ₄ , 90 °C, 2 h	0.01 (bromide)	N.D.	32
PVP-stabilized PdNPs	SM	H_2O : EtOH (3 : 1), K_3PO_4 , 90 °C, 6 h under nitrogen	0.0008 (iodide)	20 625	79
Tris-imidazolium-stabilized Pd NPs	S	DMF, piperidine, 130 °C	0.2	380	80
CPS-MNPs-NNN-Pd	S	H ₂ O/DMF (2/1), K ₂ CO ₃ , 90 °C	0.5	31	81
PdCu@Phos.Agarose	S	DMA, DABCO, 50 °C, 24 h	0.05 (0.8 mol%Cu)	77	82
Pdnp-nSTDP	S	H ₂ O, DIPEA, r.t., 2 h	0.01 (iodide)	4800	75

Table 1 Comparison of Pd-NP reported catalysts on the C-C coupling reaction

S M = Suzuki Miyaura; S = Sonogashira; H = Heck.



Fig. 7 Top: UV-visible absorption spectra (6 s intervals). Bottom: Absorption dependence on time for the catalytic reduction of 4-nitrophenol using Pd-NP-B3 as the catalyst.

appearance of 4-nitrophenol by UV-vis (Fig. 7). The reaction was complete after 36 min using 0.25 mol% of Pd-NP-B3.

Under these conditions the reaction proceeds with $k_{app} = 0.6 \times 10^{-3} \text{ s}^{-1}$. In order to compare to literature data we calculated the constant normalized k_{norm} taking into account the concentration of sodium borohydride and the quantity of Pd used. The values of k_{norm} for different catalysts recently reported in the literature are given in Table 2 and it appears that our catalyst is clearly efficient in this context.

The reduction of styrene catalysed by Pd-NP-B3 was conducted in water using two reductants: H_2 or NaBH₄. With hydrogen under a pressure of 1 bar the reaction was complete at room temperature after 3 h using 0.8 mol% of catalyst. For NaBH₄ using 6 equivalents the reaction was complete at room temperature after 3 h using 0.8 mol% of catalyst. TOF_{surf} values are identical in both reactions and correspond to 41 h⁻¹. In both cases no formation of Pd precipitates was observed. Few reports could be found in the literature concerning catalytic hydrogenation of styrene in pure water with Pd-NPs but when comparing our catalyst to some representative

 Table 2
 Comparison of NP reported catalysts on 4-nitrophenol reduction

knorm a (s ⁻¹ , mol ⁻¹ g ⁻¹) Ref. Pd-NP-B3 150 0.0006 907 020.3 This word Pd nanodendrites 27.9 0.0021 681.8 83 Au NPs 120 0.0019 21 149.9 84 Au-Ag NPs 7 0.000475 712.5 85 AuNPs 448 0.000833 8280.3 86 AuNPs@vesicle 7 0.0026 768 745.4 87 Cu NPs 167 0.000159 12 519.7 88 Fe-Q.@dextran/Pd 1000 0.00092 11 400.2 89					
Pd-NP-B3 150 0.0006 907 020.3 This word Pd nanodendrites 27.9 0.0021 681.8 83 Au NPs 120 0.0019 21 149.9 84 Au-Ag NPs 7 0.000475 712.5 85 AuNPs 448 0.000833 8280.3 86 AuNPs@vesicle 7 0.0026 768 745.4 87 Cu NPs 167 0.000159 12 519.7 88 E-O.@dextran/Pd 1000 0.00092 11 400.2 89	Catalyst	NaBH ₄ eq.	$k_{\mathrm{app}}(\mathrm{s}^{-1})$	$k_{\rm norm}^{\ a} ({\rm s}^{-1}, {\rm mol}^{-1} {\rm g}^{-1})$	Ref.
Pd nanodendrites 27.9 0.0021 681.8 83 Au NPs 120 0.0019 21 149.9 84 Au-Ag NPs 7 0.000475 712.5 85 AuNPs 448 0.000833 8280.3 86 AuNPs@vesicle 7 0.0026 768 745.4 87 Cu NPs 167 0.000159 12 519.7 88 E-O_@dextran/Pd 1000 0.00092 11 400.2 89	Pd-NP-B3	150	0.0006	907 020.3	This work
Au NPs 120 0.0019 21 149.9 84 Au-Ag NPs 7 0.000475 712.5 85 AuNPs 448 0.000833 8280.3 86 AuNPs@vesicle 7 0.0026 768 745.4 87 Cu NPs 167 0.000159 12 519.7 88 E-O.@dextran/Pd 1000 0.00092 11 400.2 89	Pd nanodendrites	27.9	0.0021	681.8	83
Au-Ag NPs 7 0.000475 712.5 85 AuNPs 448 0.000833 8280.3 86 AuNPs@vesicle 7 0.0026 768 745.4 87 Cu NPs 167 0.000159 12 519.7 88 Fe-O.@dextran/Pd 1000 0.000092 11 400.2 89	Au NPs	120	0.0019	21 149.9	84
AuNPs 448 0.000833 8280.3 86 AuNPs@vesicle 7 0.0026 768 745.4 87 Cu NPs 167 0.000159 12 519.7 88 Fe-O_@dextrap/Pd 1000 0.000092 11 400.2 89	Au-Ag NPs	7	0.000475	712.5	85
AuNPs@vesicle 7 0.0026 768 745.4 87 Cu NPs 167 0.000159 12 519.7 88 Fe-O_@dextrap/Pd 1000 0.000092 11 400.2 89	AuNPs	448	0.000833	8280.3	86
Cu NPs 167 0.000159 12 519.7 88 Fe-O.@dextran/Pd 1000 0.000092 11 400.2 89	AuNPs@vesicle	7	0.0026	768 745.4	87
Fe ₂ O ₂ @dextran/Pd 1000 0 000092 11 400 2 89	Cu NPs	167	0.000159	12 519.7	88
10304@dextimine 1000 0.000092 11400.2 09	Fe ₃ O ₄ @dextran/Pd	1000	0.000092	11 400.2	89

 ${}^{a}k_{norm}$ values were calculated from k_{app} normalized to the molar concentration of NaBH₄ and the Pd quantity.

results (Table 3) it could be stated that activities similar to the best reported systems are observed.

Cycloisomerization of pentynoic acid. Pentynoic acid cycloisomerization was evaluated in water with 0.05 mol% of Pd-NP-B3 as a catalyst followed by GC. Several conditions were

 Table 3
 Comparison of Pd-NP reported catalyst efficiency and quantity on the styrene reduction reaction

Catalyst	Conditions	mol% Pd for complete conversion	$\operatorname{TOF}\left(h^{-1}\right)$	Ref.
Pd-NP-B3	H ₂ O, 3 h, 1 bar H ₂ or 6 eq. NaBH ₄	0.8	41	This work
NHC PdNPs	$H_2O, 3h, 1$ bar H_2	0.42	N.D.	30
Pd ⁰ @g-Fe ₂ O ₃	H ₂ O, 3 h, 1 bar H ₂	1	100	71
IL stabilized	H ₂ O, 1.5 h, 50 °C, 4	0.4	N.D.	34
Pd NPs	bar H ₂			

All reagents were purchased from Fisher Scientific and used

without further purification. Compounds 1, 3, 4 and 5 were synthesized using a protocol adapted from the study by

Aufaure et al.⁵⁴ (see the ESI[†]). Compound 2 was obtained by

following the protocol described by Kieczykowski et al.92

Compound 7 (PEOMA-co-MAPC1 ACID) was purchased from

Specific Polymers, France. Nanopure water (conductivity of

0.06 mS cm⁻¹) obtained from a Millipore Gradiant Elix-3A10

system was used to prepare the sample solutions.

Transmission electron microscopy (TEM) was used to charac-

terize the nanoparticles. TEM images were recorded using a

evaluated and optimal conditions were obtained by running the reaction at 40 °C for 60 min. Under these conditions, the conversion was complete without any traces of the ketoacid byproduct formation. If the reaction was prolonged or the temperature was increased the ketoacid byproduct starts to form. To produce the ketoacid with a complete conversion the reaction should be run at 90 °C for 3 h. Compared to previous work our catalyst appears competitive, as it was able to produce the cycloisomerization product selectively under mild conditions without addition of any base or co-catalyst and with a low loading of Pd (2 times less Pd mol% than the best catalyst described so far).⁷² Moreover, it was also able to realize the subsequent hydrolysis of the cycloisomerization product into the ketoacid by simply increasing the temperature and the length of reaction time.

Conclusions

In conclusion, the preparation of stable Pd-NPs in aqueous media was developed. The proposed synthesis is environmentally friendly: using microwaves, no toxic solvents, biocompatible reductants and commercial and/or nontoxic stabilizers. Phosphonic acids were for the first time used as stabilizers for catalytic Pd NPs. This family of (generally) water soluble molecules is highly valuable due to the fact that they allow a great variety of chemical structures, with molecules produced at an industrial level and for some compounds relatively low toxicity (some are FDA approved drugs) compared to other stabilizers. The synthesized Pd-NPs were able to catalyse up to 6 different organic reactions in an aqueous medium under benign conditions. Moreover, the possibility to finely tune the stabilizer constitution permit us to improve the catalysis efficacy by allowing the surface mass transfer enhancement of organic substrates to the surface. The best catalysts enable highly efficient organic reactions in aqueous media with quantities of Pd down to the ppm level without the need for extra surfactants or co-catalysts. Evaluations are still ongoing on the exemplification of each reaction and on other reaction types but our preliminary results are highly encouraging. In addition, these preliminary results have to be also emphasized by the simplicity and eco-compatibility of the synthesis of the NP catalysts requiring mild conditions (synthesis at mild temperature, under aerobic conditions and in water) with benign and simple reactants. Moreover, another important aspect is the stability of the catalyst in time as the solutions of Pd NPs are stable by simply storing them in water and under aerobic conditions at 4 °C and could be used more than 6 months after their preparation without any loss in catalytic ability. Finally, the shape control and formation of anisotropic Pd-NPs can have interesting catalytic activities in other areas which would be further studied.^{78,90} Now transposing the synthesis to other metallic NPs or even alloys by using different metallic salts is also envisioned. In addition, such stable aqueous metallic-NPs could also find applications in other fields such as in nanomedicine.91

JEOL JEM-2100F instrument (Japan) at an acceleration voltage of 200 kV and visualised with a CCD camera. The sample was dispersed in ultra-pure water, added drop-wise onto a copper mesh grid coated with an amorphous carbon film and allowed to air-dry. Transmission electron microscopy (TEM) images were recorded using a JEOL JEM-2100F instrument (Japan) at an acceleration voltage of 200 kV and visualised with a CCD camera. The crystallinity of the NPs was analysed using selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM). The sample was prepared by depositing a drop of the solution onto a copper mesh grid coated with an amorphous carbon film and allowed to air-dry. Infrared spectra were recorded with an Agilent Technologies Cary 600 Series FTIR. Spectra were recorded through the form of thin KBr pellets. X-ray photoelectron spectroscopy (XPS) analyses were performed using an ESCA+ spectrometer (Omicron NanoTechnology), equipped with a monochromatized aluminum X-ray source (powered at 20 mA and 14 kV) and a MCD 128 channeltron detector. Charge stabilization was insured using the CN10 device with an emission current of 5.0 µA and a beam energy of 1 eV. Analyses were performed in the sweeping mode; the resulting analyzed area was about 1 mm in diameter. A pass energy of 20 eV was used for narrow scans. Under these conditions, the full width at half maximum (FWHM) of the Ag 3d_{5/2} peak of a clean silver reference sample was about 0.6 eV. The pressure in the analysis chamber was around 10⁻¹⁰ torr. The photoelectron collection angle, θ , between the normal to the sample surface and the analyzer axis was 45°. The following sequence of spectra was recorded: survey spectrum, C 1s, N 1s, O 1s, P 2p, Na 1s, Pd 3d, Cl 2p, and Si 2p. The binding energy scale was set by fixing the C 1s component due to carbon only bound to carbon and hydrogen at 284.8 eV. The data treatment was performed with CasaXPS software (Casa Software Ltd, UK). DLS and ζ potential analyses were performed on a nano ZS (red badge) ZEN3600 Zetasizer at neutral pH. UV-visible spectra were recorded on a Varian Cary 50 Scan UV-Visible spectrophotometer. EDX microanalyses were performed using a TM 3000 tabletop microscope equipped with a Swift EDX-ray 3000 microanalysis system (Oxford Instruments). Samples were deposited as powder on a copper surface, and data were collected using a 15 kV accelerating voltage and studying the ratio of P vs. Pd. Gas

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Chromatography (GC) analyses were performed using a PerkinElmer Autosystem XL instrument equipped with an autosampler and a flame ionization detector and a 30 m ATTM-1ht capillary column (0.25 mm diameter, 0.1 µm film thickness), using nitrogen (2 mL min^{-1}) as a carrier gas. The following parameters are used: $T_{\text{injector}} = 350 \text{ °C}$ and $T_{\text{column}} = 40 \text{ °C}$ (2 min) and 40-250 °C (20 °C min⁻¹). ¹H NMR spectra (400 MHz) and proton-decoupled ¹³C NMR spectra (100.63 MHz) were recorded on a Bruker Avance III 400 spectrometer. Chemical shifts are reported in parts per million (ppm) on the δ scale. The residual solvent peaks were used as internal references (¹H NMR: CHCl₃ 7.26 ppm; ¹³C NMR: $CDCl_3$ 77.2 ppm). Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintuplet, and m = multiplet and coupling constant(s) are given in Hz. Turnover frequencies were calculated considering the number of Pd atoms on the surface for reactions at a low conversion rate (Graham).

General preparation of Pd-NPs

In a 10 mL vial, 2 mL of distilled water, 80 μ L of a water solution of Na₂PdCl₄ (20 mM) and 180 μ L of bisphosphonic acid solution in water (40 mM compounds 1–5) are mixed (for compounds 6 and 7, 360 μ L of a 40 mM solution and 180 μ L of a 170 mg mL⁻¹ solution are used). Then 40 μ L of a solution of sodium ascorbate (17.6 mg mL⁻¹) were added and the mixture was heated on a microwave apparatus (Monowave 300, Anton Paar GmbH) for 30 min at 80 °C using a ruby thermometer (step 1: heat as fast as possible to 100 °C and step 2: hold at 100 °C for 30 min with the stirring speed being 1200 rpm for both steps).

General procedure for the Suzuki–Miyaura cross coupling reaction of 4-tolylboronic acid with 4-iodonitrobenzene with Pd-NPs

In a 10 mL MW vial, 23 µL of an aqueous solution of Pd-NPs $([Pd] = 0.02 \,\mu\text{M})$ was added to 1 mL of water. 49.8 mg of 4-iodonitrobenzene (0.20 mmol), 30 mg of 4-tolylboronic acid (0.22 mmol) and 400 µL of a 0.1 M K₂CO₃ solution (0.4 mmol) were then added. The glass walls of the vial were rinsed with 1 mL of ethanol and a cap was fixed on the top of the vial. The vial was heated on a microwave apparatus (Monowave 300, Anton Paar GmbH) for 30 min at 80 °C using a ruby thermometer (step 1: heat for 2 min to 80 °C and step 2: hold at 80 °C for 28 min with the stirring speed being 1200 rpm for both steps). After cooling the solution, 1 mL of diethyl ether or ethyl acetate was added and the organic layer was extracted 5 times. The product was then isolated by evaporation and purified by simple filtration over silica when conversion was complete or purified by silica gel column chromatography using ethyl acetate hexane mixtures when starting halogenated reactants remained un-reacted. ¹H NMR (CDCl₃, 25 °C): δ = 8.28 (d, J = 8.8 Hz, 2H); 7.72 (d, J = 8.8 Hz, 2H); 7.53 (d, J = 8.8 Hz, 2H); 7.30 (d, J = 8.8 Hz, 2H); 2.42 (s, 3H) ppm. ¹³C{¹H}NMR (CDCl₃, 25 °C): *δ* = 147.8; 147.0; 139.3; 136.0; 130.0; 127.7; 127.4; 124.3; 21.4 ppm.

General procedure for the Sonogashira reaction of phenylacetylene with 4-iodonitrobenzene with Pd-NPs

In a 10 mL MW vial, 43.5 µL of an aqueous solution of Pd-NPs ([Pd] = 0.695 mM) was added to 600 μ L of water. 49.8 mg of 4-iodonitrobenzene (0.20 mmol), 24 µL of phenylacetylene (0.22 mmol) and 400 µL of a 1 M K₂CO₃ solution were then added. The glass walls of the vial were rinsed with 1 mL of ethanol and a cap was fixed on the top of the vial. The vial was heated with an oil bath or on a microwave apparatus for 30 min at 80 °C using a ruby thermometer (step 1: heat for 2 min to 80 °C and step 2: hold at 80 °C for 30 min with the stirring speed being 1200 rpm for both steps). After cooling the solution 1 mL of diethyl ether or ethyl acetate was added and the organic layer was extracted 5 times. The product was then isolated by evaporation and purified by simple filtration over silica when conversion was complete or purified by silica gel column chromatography using ethyl acetate hexane mixtures when starting halogenated reactants remained unreacted. ¹H NMR (CDCl₃, 25 °C): δ = 8.23 (d, J = 9 Hz, 2H); 7.67 (d, J = 8.8 Hz, 2H); 7.56 (m, 2H); 7.39 (m, 3H) ppm. ¹³C{¹H} NMR (CDCl₃, 25 °C): δ = 146.9; 132.3; 131.9; 130.3; 129.3; 128.6; 123.7; 122.1; 94.7; 87.5 ppm.

General procedure for the Heck reaction of methyl methacrylate with 4-iodonitrobenzene with Pd@-NPs

In a 10 mL MW vial, 287.7 µL of an aqueous solution of Pd-NPs ([Pd] = 0.695 mM) was added to 400 µL of water. 49.8 mg of 4-iodonitrobenzene (0.20 mmol), 27 µL of methyl methacrylate (0.2 mmol) and 400 µL of a 1 M K₂CO₃ solution were then added. The glass walls of the vial were rinsed with 1 mL of ethanol and a cap was fixed on the top of the vial. The vial was heated on a microwave apparatus for 2 h at 80 °C using a ruby thermometer (step 1: heat for 2 min to 80 °C and step 2: hold at 80 °C for 2 h with the stirring speed being 1200 rpm for both steps). After cooling the solution 1 mL of diethyl ether or ethyl acetate was added and the organic layer was extracted 5 times. The product was then isolated by evaporation and purified by simple filtration over silica when conversion was complete or purified by silica gel column chromatography using ethyl acetate hexane mixtures when starting halogenated reactants remained un-reacted. NMR ¹H (CDCl₃, 25 °C): δ = 8.24 (d, J = 8.8 Hz, 2H); 7.71 (d, J = 16.2 Hz, 1H); 7.66 (d, J = 8.8 Hz, 2H); 6.56 (d, I = 16.2 Hz, 2H); 3.83 (s, 3H) ppm. NMR ${}^{13}C{}^{1}H{}$ $(CDCl_3, 25 \ ^{\circ}C): \delta = 166.7; 148.5; 142.0; 140.5; 128.6; 124.5;$ 122.1; 52.1 ppm.

General procedure for the reduction of 4-nitrophenol with Pd-NPs

The reaction was performed in a 3 mL quartz cell (Hellma) to perform the kinetic measurements. The solutions of 4-nitrophenol and NaBH₄ were freshly prepared before each measurement, without purging with N₂, and 30 µL of 4-nitrophenol (7.4 \times 10⁻² mM) solution were added to the reaction medium (2.8 ml of water), with 200 µL of sodium borohydride (0.167 M, 150 eq.). The solution was then left undisturbed for some seconds, after

which 20 μL of NP-Pd solution (0.028 mM) was added. Immediately after the addition of Pd nanoparticles, time-dependent absorption spectra were recorded at 6 s intervals.

General procedure for the reduction of styrene with Pd-NPs

5.75 mL of the solution of Pd-NP-B3 ([Pd] = 0.68 mM) were added in a 50 mL boiling flask and purged with H₂ for 3 min, and 57 μ L of styrene (0.5 mmol) was added to the reaction medium and purged a second time with H₂ for 4 min. Then, immediately the flask is closed to perform the reduction reaction at room temperature and 1200 rpm for 3 h. The reaction evolution was followed by gas chromatography using ethyl acetate as the solvent.

In the case of use of NaBH₄ as a reductant, 114 mg of sodium borohydride (6 eq.) were added in a 50 mL boiling flask with 5.75 mL of Pd-NP-B3 ([Pd] = 0.68 mM). The solution was stirred at 1200 rpm for one minute, after which 57 μ L of styrene (0.5 mmol) was added to the reaction medium. The reaction was performed at room temperature for 3 h. The reaction evolution was followed by gas chromatography using ethyl acetate as the solvent.

General procedure for the cycloisomerization reaction with Pd-NPs: cycloisomerization product (5-methylenedihydrofuran-2 (3*H*)-one)

In a 10 mL MW vial, 115 µL of an aqueous solution of Pd-NPs ([Pd] = 0.695 mM) was added to 500 µL of water. 19.6 mg of pentynoic acid (0.20 mmol) was then added and a cap was fixed on the top of the vial. The vial was heated on a microwave apparatus for 60 min at 40 °C using a ruby thermometer (step 1: heat for 2 min to 40 °C and step 2: hold at 40 °C for 60 min with the stirring speed being 1200 rpm for both steps). After cooling the solution, 1 mL of diethyl ether or ethyl acetate was added and the organic layer was extracted 5 times. The high volatility of the compound prevented accurate determination of the isolated yield. ¹H NMR (400 MHz, CDCl₃) δ 4.72 (dd, *J* = 4.5, 2.2 Hz, 1H), 4.30 (dd, *J* = 4.3, 1.8 Hz, 1H), 2.91–2.81 (m, 2H), 2.70–2.63 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 175.0, 155.7, 88.7, 28.0, 25.1. Colourless oil.

Ketoacid by-product (4-oxopentanoic acid): 19.6 mg of pentynoic acid (0.20 mmol) was added in a 10 mL MW vial with 500 µL of water and 143 µL of an aqueous solution of Pd-NPs (0.695 mM). Subsequently, the vial was sealed with a cap and heated on a microwave apparatus for 180 min at 90 °C using a ruby thermometer (step 1: heat for 2 min to 90 °C and step 2: hold at 90 °C for 180 min with the stirring speed being1200 rpm for both steps). After cooling the solution, 1 mL of diethyl ether or ethyl acetate was added and the organic layer was extracted 5 times. ¹H NMR (400 MHz, CDCl₃) δ 9.32 (s, 1H), 2.73 (t, *J* = 6.5 Hz, 1H), 2.59 (t, *J* = 6.5 Hz, 1H), 2.17 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 206.8, 178.6, 37.7, 29.8, 27.8. Colourless oil.

Conflicts of interest

There are no conflicts to declare.

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