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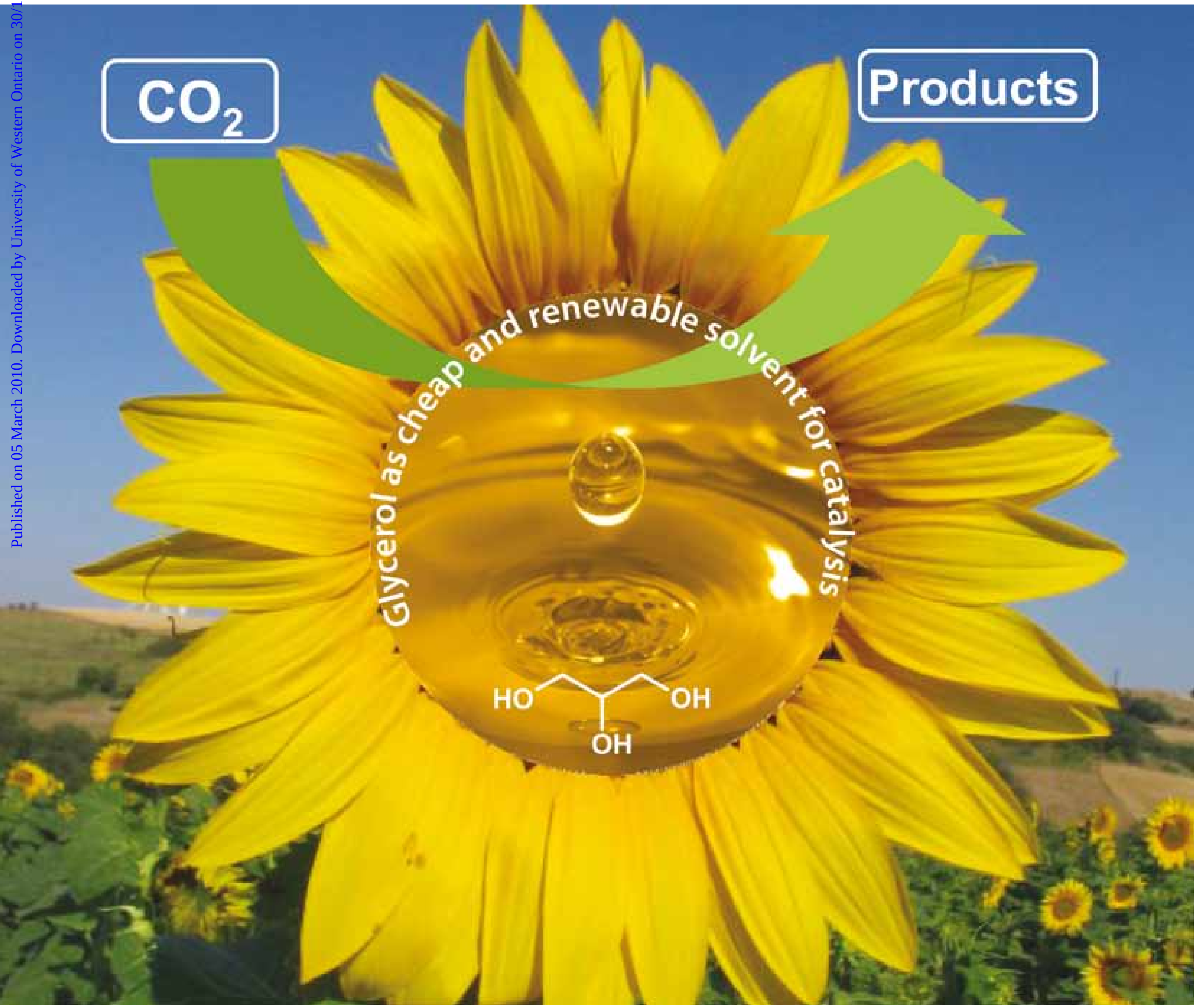

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Glycerol as a cheap, safe and sustainable solvent for the catalytic and regioselective β,β-diarylation of acrylates over palladium nanoparticles †‡

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Herein we show that glycerol can be considered as a promising cheap and green solvent for the regioselective β,β-diarylation of alkenes. Whereas this reaction is generally catalyzed under an inert atmosphere by expensive phosphine or carbene-palladium complexes, we show here that the diarylation of alkenes can be conveniently achieved in glycerol in the presence of air-stable palladium nanoparticles. These palladium nanoparticles were stabilized over a sugar-based surfactant derived from biomass. By an adjustment of the reaction temperature, we were able to control the mono- and diarylation step of alkenes, thus offering a convenient route to unsymmetrical diarylated alkenes. At the end of the reaction, the diarylated alkenes were cleanly and selectively extracted from the glycerol-palladium catalytic phase using supercritical carbon dioxide, thus affording a convenient purification work-up. Within the framework of green chemistry, this work combines (i) catalysis in a cheap, safe and sustainable medium, (ii) easily made and air-stable palladium nanoparticles as the catalyst, and (iii) a clean and selective extraction of the reaction products with supercritical carbon dioxide.

Introduction

The palladium-catalyzed Mizoroki–Heck coupling is a reaction of fundamental importance in organic chemistry and has broad applications from the manufacture of basic chemicals to the preparation of fine pharmaceuticals. In this context, plenty of work have been focused on this reaction.[1] Even if spectacular results have been reported over the last 30 years, this work was mainly applicable to the monoarylation of alkenes, and examples of diarylation remain scarce. Diarylated alkenes are valuable chemical platforms that are used in many processes, and their one-pot synthesis still represents a challenging task today.

In the current literature, phosphine[2–5,6d,e] and carbene[6a–c] palladium complexes have been reported as efficient catalysts for the diarylation of various alkenes, such as vinyl silane,[2] boronate,[3] 2-pyrimidylsulfide,[4] ethers[5] and acrylates.[6] Although these catalysts provided excellent results in many respects, they are unfortunately expensive and require an inert atmosphere.

The diarylation of acrylate derivatives generally occurs at a higher temperature (120–140 °C) than the monoarylation step. Therefore, these reactions are generally carried out in high boiling point solvents such as DMF,[5b,6e] in ionic liquids[6a–c] or under pressure.[6d] Within the framework of green chemistry, Botella and Najera investigated the β,β-diarylation of acrylate derivatives in water and in the presence of an oxime-derived palladacycle.[7] At 120 °C (under pressure of water), they successfully achieved the β,β-diarylation of *tert*-butyl acrylate. If this work indisputably offered a greener route to the synthesis of disubstituted acrylate derivatives, this method is only applicable to the *tert*-butyl acrylate. Indeed, in water, the authors pointed out that other acrylate derivatives were partially hydrolyzed, making difficult the isolation of the disubstituted alkenes in good yield.[7a]

Recently, we and the group of Wolfson have reported that glycerol may be considered as a promising cheap and green solvent for catalysis.[8,9] Indeed, like water, glycerol is highly hydrophilic, non-toxic, cheap (0.5 € Kg^{-1}, sometimes even cheaper than water!), non-flammable and available on a large scale from biomass (hydrolysis of vegetable oils, production of glycerol = 1.5 Mt in 2008). Moreover, glycerol exhibits a high boiling point and a low vapour pressure (<1 mmHg at 50 °C), making easier and safer the development of catalytic processes at a temperatures higher than 100 °C. In 2009, the number of publications dealing with the possible use of glycerol as a sustainable solvent for catalysis significantly increased, thus showing the interest of the scientific community in this medium.[10]

Here, we wish to show that the regioselective β,β-diarylation of acrylate derivatives can be conveniently achieved in glycerol in the presence of easily-made palladium nanoparticles stabilized over a sugar-based surfactant derived from biomass. To the best of our knowledge, this is the first example of the β,β-diarylation of alkenes over palladium nanoparticles. This work

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† The synthesis and characterization of aminopolysaccharide (AP) has been already described in a previous paper.[8b]

‡ Electronic supplementary information (ESI) available: Product characterizations and ^1H NMR spectra. See DOI: 10.1039/b925021b

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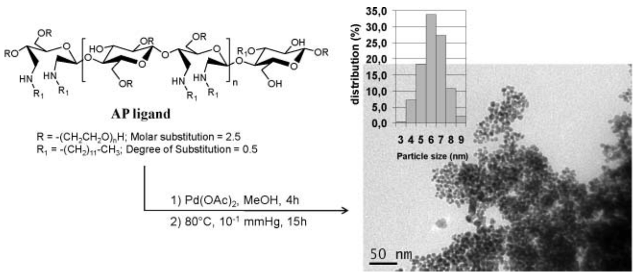
opens access to a wide range of symmetrical and unsymmetrical trisubstituted alkenes in air and without the assistance of any phosphine or carbene ligands, like is generally the case. It should be noted that, at the end of the reaction, the trisubstituted alkenes were cleanly and selectively extracted from the catalytic phase with supercritical carbon dioxide (scCO_2), thus affording a very convenient purification work-up. Within the framework of green chemistry, this work gathers (i) catalysis in a cheap and sustainable media, (ii) the utilization of air-stable palladium nanoparticles stabilized over a bio-based surfactant, and (iii) a clean and selective extraction of the reaction products with scCO_2.

Results and discussion

Recently, we reported the synthesis of a new sugar-based surfactant called aminopolysaccharide (AP), which has been found particularly efficient for catalysis in glycerol.[8b] Indeed, owing to its surfactant properties, we showed that AP was able to increase the solubility of organic reactants in the glycerol phase, thus resulting in a significant increase of the reaction rate. In a continuation of our efforts, we decided to use AP as a ligand for the coordination of palladium. The coordination of palladium onto AP was performed by mixing the AP ligand with a methanolic solution of $Pd(OAc)_2$ (0.3 g L^{-1}). The mixture was stirred for 4 h and the methanol then gently removed under reduced pressure. The recovered black solid was placed in an oven at 70 °C and 10^{-1} mmHg for 15 h, yielding the corresponding surfactant-combined catalyst Pd/AP. ICP analysis revealed a Pd content of 1.5 wt%. Further inspection by transmission electronic microscopy showed that the amphiphilic AP was able to stabilize some Pd nanoparticles with an average size of 6 nm (Scheme 1).

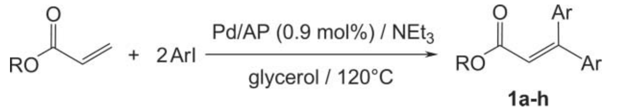


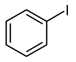
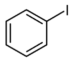
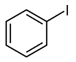
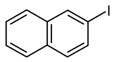
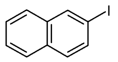
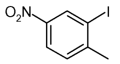
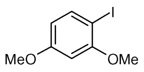
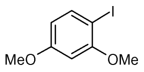
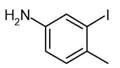
Scheme 1 Synthesis of the Pd/AP catalyst.

1. Symmetrical β,β-diarylation of acrylate derivatives

In a first set of experiments, we tested the catalytic activity of the Pd/AP catalyst, using iodobenzene and cyclohexylacrylate as model substrates. The reaction was performed in the presence of 0.9 mol% of palladium nanoparticles stabilized over AP and triethylamine. To our delight, when the reaction was heated at 120 °C in the presence of 2 equiv. of iodobenzene, a double arylation of cyclohexyl acrylate took place, and **1a** was obtained in 67% yield (Table 1, entry 1). It should be noted that, at 120 °C, biphenyl (<10% yield) was also produced as a side product. Surprisingly, under stoichiometric conditions, no monoarylated adduct was detected, despite the formation of biphenyl. Further inspections revealed that the monoarylated intermediate was actually strongly retained within the amphiphilic framework of the Pd/AP catalyst (see the experimental section for more details§). With the aim of increasing the yield of **1a**, 3 equiv. of

Table 1 β,β-Diarylation of acrylate derivatives in glycerol



Entry	R	ArI	Product	Yield (%)[a]
1[b]	Cyclohexyl		**1a**	67
2	Cyclohexyl		**1a**	92
3	Butyl		**1b**	95
4	Cyclohexyl		**1c**	96
5	Butyl		**1d**	70
6	Cyclohexyl		**1e**	85
7[c]	Butyl		**1f**	80
8[c]	Cyclohexyl		**1g**	86
9	Cyclohexyl		**1h**	93

[a] Isolated yield after 30 h of reaction, 3 equiv. of aryl iodides and triethylamine were used. [b] 2 equiv. of iodobenzene was used. [c] Reaction performed at 80 °C.

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§ **General procedure for the synthesis of Pd/AP:** In a typical procedure, the AP ligand (DS = 0.5, 1.6 mmol N g^{-1}, 100 mg) was dissolved in 10 mL of methanol. Then, 3.2 mg of $Pd(OAc)_2$ dissolved in 10 mL of methanol was added dropwise to the methanolic solution of AP. The resulting mixture was then stirred for 4 h at room temperature. After this period, the solution was placed in a rotary evaporator and the methanol gently removed under reduced pressure (15 mmHg). The recovered black solid was finally placed in an oven at 70 °C (10^{-1} mmHg) for 24 h, affording the corresponding Pd/AP. ICP measurements revealed a Pd content of 1.5%. As mentioned in main text, the AP ligand was able to stabilise some palladium nanoparticles with an average size of 6 nm. The average particle size was determined on the basis of 500 nanoparticles. **General procedure for the β,β-diarylation of acrylate derivatives (Table 1)**: In a 15 mL glass autoclave, acrylate (3 mmol), aryl iodide (9 mmol), triethylamine (18 mmol), glycerol (2.5 mL) and Pd/AP (200 mg, 0.009 equiv.) were stirred under aerobic conditions at 120 °C for 30 h. The reaction progress was monitored by gas chromatography. **Note:** As mentioned in the main text, 3 equiv. of aryl iodides were necessary due to the side formation of biphenyl (<10% yield), which is a known side product in palladium-catalyzed Heck coupling. When stoichiometric amounts of iodobenzene (6 mmol), butyl acrylate (3 mmol) and triethylamine (6 mmol) were heated in 2.5 mL of

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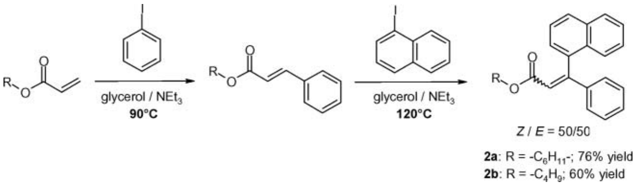
iodobenzene were used. As expected, under these conditions, the yield of **1a** was raised from 67 to 92% yield (Table 1, entry 2).

As summarized in Table 1, many aryl iodides were tested in glycerol and, in all cases, the diarylated alkenes **1b-h** were successfully obtained in air with a yield range of 70–96%. Interestingly, contrary to what was observed in water, the ester moiety was found to be highly stable in glycerol and, in all cases, no transesterification reaction between glycerol and the ester moiety occurred (triethylamine is not basic enough to catalyze this reaction at 120 °C). Note that, in accordance with most previous works on the diarylation of alkenes, this catalytic process was most efficient with aryl iodides. Indeed, the utilization of aryl bromides or chlorides unfortunately slowed down the reaction rate to unacceptable levels. It is also noteworthy that the reaction is highly regioselective, since only β,β-diarylation occurred in glycerol.

We also carefully checked the stability of the glycerol under our conditions (NMR, GC). To this end, glycerol (2.5 mL) was mixed with triethylamine (9 mmol) and 200 mg of Pd/AP (Pd: 0.9 mol%), and heated at 120 °C for 48 h. No product resulting from the palladium-catalyzed degradation of glycerol was detected, indicating the stability of glycerol under our conditions (see the ^{1}H NMR spectra in the ESI, Scheme S1 and S2‡). This result is in accordance with previous works described in the literature.[11]

2. Unsymmetrical β,β-diarylation of acrylate derivatives

We then moved onto the synthesis of unsymmetrical disubstituted alkenes, which represent an even more challenging task. Unfortunately, the addition of two different aryl iodides at 120 °C in the same reaction pot afforded a mixture of symmetrical and unsymmetrical disubstituted alkenes. Considering that the monoarylation of alkenes easily takes place at 80 °C in glycerol with commonly used palladium complexes, it occurred to us that the mono- and diarylation of alkenes could be closely controlled in glycerol by adjustment of the reaction temperature. To this end, the catalytic reaction was first performed at 90 °C with iodobenzene. As expected, at 90 °C, only the monoarylation took place. Then, iodonaphthalene (2 equiv.) was directly added to the crude mixture and the temperature raised to 120 °C. To our delight, under these conditions, the unsymmetrical β,β-diarylated alkenes **2a** and **2b** were obtained in 60–76% yield, thus providing a cost-efficient, safe and environmentally friendly route to more valuable substrates (Scheme 2).



Scheme 2 Unsymmetrical β,β-diarylation of acrylate derivatives in glycerol.

3 Extraction of the reaction products with scCO$_2$

Next, we examined the extraction of the reaction products from the glycerol phase. As is the case for ionic liquids, glycerol is a high boiling point solvent and its removal by distillation is not conceivable. Therefore, the extraction of the reaction products from the glycerol phase is an important issue that must be addressed. Recently, we found that long alkyl chain esters can be directly extracted from glycerol by simple phase decantation, thus avoiding the assistance of volatile organic solvents.[8b] However, in the present case, this process is not applicable, since, in the presence of the amphiphilic Pd/AP catalyst, the reaction products remain soluble in glycerol. Therefore, the assistance of an extraction solvent was found to be necessary to recover the product from the reaction. Among all of the tested extraction solvents, we found that scCO$_2$ was by far the most efficient solvent to selectively extract the β,β-diarylated products from the glycerol-Pd/AP catalytic phase. Indeed, other tested solvents such as dichloromethane, ethyl acetate and toluene, among others, led to the concomitant extraction of the reaction products and the Pd/AP catalyst, thus involving further purification steps.

In order to get as close as possible to industrial apparatus, scCO$_2$ extractions were performed on a SEPAREX SF200 pilot, comprising an extraction vessel (200 mL) followed by a cascade of three separators connected to the extractor outlet (see the ESI for the apparatus, Fig. S2‡). In these experiments, the β,β-diarylation of butyl acrylate with iodobenzene was chosen as the model reaction. Compared to the above-described experiments, this reaction was scaled-up and stoichiometric amounts of iodobenzene (96 mmol), butyl acrylate (48 mmol) and triethylamine (96 mmol) were used (Pd/AP = 0.9 mol%, *i.e.* 3.1 g) in order to determine the efficiency of the whole process. Under these conditions, 95% of the iodobenzene was consumed after 30 h of reaction and 10.1 g of **1b** (75% yield) was produced. The mixture was then introduced into the extractor and scCO$_2$ extractions were performed with a scCO$_2$ flow of 40 g min^{-1} at 50 °C and 250 bar. Samples were collected from the separators every 30 min and analyzed (Fig. 1). Note that in our apparatus, the scCO$_2$ was recycled in order to avoid the excessive utilization of CO$_2$.

To our great delight, after 420 min of continuous extraction with scCO$_2$, 8.6 g of products were cleanly recovered from the

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glycerol at 120 °C, 0.56 g of **1b** (67% yield), 0.05 g of biphenyl (10% yield) and 0.04 g of unreacted iodobenzene were isolated after extraction with dichloromethane and purification over silica gel. Surprisingly, despite biphenyl being produced, no trace of the monoarylated adduct was detected. Further inspection revealed that the monoarylated adduct was actually strongly encapsulated by the Pd/AP catalyst. Indeed, extensive extraction of the glycerol phase with a large excess of hot toluene (6 × 10 mL) led to the release of the monoarylated adduct encapsulated by the Pd/AP, and 0.2 g of the monoarylated adduct (28% yield) was recovered. For the moment, we cannot explain the selective encapsulation of the monoarylated adduct, as compared to **1b**. It should be noted that the encapsulation of the intermediate mono-Heck adduct is more pronounced when using butyl acrylate derivatives than with cyclohexyl acrylate. **General procedure for the unsymmetrical β,β-diarylation of acrylate derivatives (Scheme 2)**: In a 15 mL glass autoclave, acrylate derivatives (3 mmol), iodobenzene (3 mmol), triethylamine (6 mmol), glycerol (2.5 mL) and Pd/AP (200 mg, 0.009 equiv. of Pd) were stirred under aerobic conditions at 90 °C for 24 h. Then, iodonaphthalene (6 mmol) and triethylamine (12 mmol) were added to the crude mixture, and the temperature was raised to 120 °C. The reaction progress was monitored by gas chromatography.

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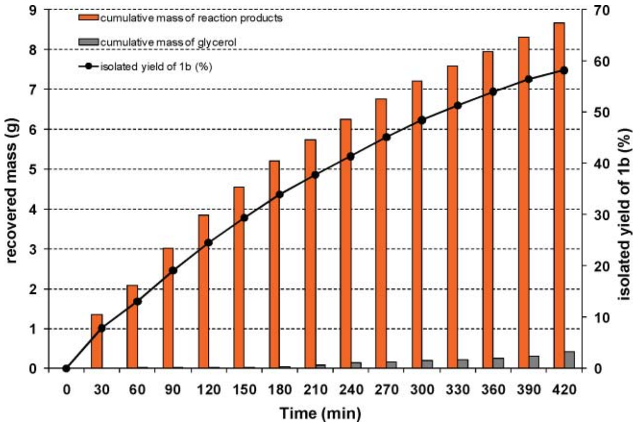

Fig. 1 The extraction of **1b** with scCO$_2$ at 40 g min^{-1}, 50 °C and 250 bar.

glycerol–Pd/AP catalytic phase and only 0.4 g of contamination with glycerol occurred. The extraction here was rather long because the reaction products were strongly retained in the glycerol phase by the amphiphilic Pd/AP catalyst. Even if the recovered products were contaminated with 4 wt% of glycerol, the total removal of glycerol from the extracted products could be easily performed by simple phase decantation (in the absence of the Pd/AP catalyst,[12] glycerol is not miscible with **1b**), thus considerably increasing the interest in using glycerol as the solvent (Fig. 2).

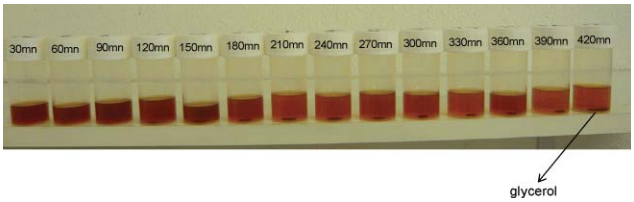

Fig. 2 Pictures of the extracted products with scCO$_2$. Note that in order to clearly show the contamination with glycerol, a few drops of ethyl acetate were added to the collected vials before taking the pictures. However, in this work, no organic solvent was used and the glycerol could be directly removed by simple centrifugation without the assistance of any organic solvent.

The solubility of glycerol in CO$_2$ under high pressure has been estimated thanks to the equation of Chrastil,[13] which correlates the solubility of solids and liquids in supercritical gases with the density of the gas. Under our conditions, we found that the solubility of glycerol in scCO$_2$ was 40 times lower than that of water (0.06 Kg m^{-3} for glycerol *vs.* 2.39 Kg m^{-3} for water; see the ESI for the calculation‡).

The recovered extracted products were then fully analyzed. The extracted products (8.6 g) contained 7.8 g of **1b** (60% isolated yield), which corresponds to an extraction efficiency of 77%. The molar purity of the recovered **1b** was 86% (contamination of **1b** with 0.4 g of unreacted iodobenzene and 0.4 g of biphenyl). Note that if the reaction was heated up to totally consume the iodobenzene, iodobenzene could no longer be co-extracted with **1b**; in this case, the molar purity of **1b** reached 93%. As expected, a decrease of the scCO$_2$ flow from 40 to 15 g min^{-1} decreased the extraction efficiency from 77 to 55%, while the glycerol contamination remained similar to that observed above at 40 g min^{-1}.

Even if the scCO$_2$ allows the convenient and selective extraction of **1b** from the glycerol-Pd/AP phase, the possible recycling of the catalytic phase remains particularly difficult. Indeed, in the typical case of palladium Heck couplings, an unavoidable accumulation of salts occurs cycle after cycle, making more and more difficult the dissolution of the reactants from the glycerol phase. Consequently, as previously observed in water or ionic liquids, a gradual decrease of the reaction rate is observed cycle after cycle (see the recycling experiments in the ESI, Fig. S1‡). Note that the stabilization of palladium nanoparticles over a solid support would provide greater means to recover the catalyst from the glycerol phase and then to reuse it. This aspect is now the topic of our investigations and will be reported in due course.

Conclusions

We report here that the regioselective symmetrical and unsymmetrical β,β-diarylation of acrylate derivatives can be conveniently performed in cheap and safe glycerol. Whereas expensive and air-sensitive palladium complexes are generally required to achieve this reaction, we have shown here that the β,β-diarylation of acrylate derivatives can be catalyzed in glycerol over air-stable palladium nanoparticles. These palladium nanoparticles were easily prepared using a sugar-based surfactant derived from biomass. Interestingly, we found that the produced diarylated alkenes could be selectively extracted from the catalytic phase using scCO$_2$, thus offering (i) a simple work-up procedure and (ii) an alternative to the extensive utilization of volatile organic solvents. We are fully convinced that this combination of glycerol and scCO$_2$ will provide new tools for the design of greener catalytic processes, and this aspect is now under investigation in our group.

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