The Sonogashira cross-coupling reaction is a great procedure for C-C bond formation between vinyl or aryl halides and terminal alkynes (Sonogashira, Tohda and Hagihara, 1975; Takahashi et al., 1980; Sonogashira, 2002). Sonogashira, Tohda and Hagihara (1975) recognised that the addition of copper(I) iodide significantly accelerates the alkenylation reaction that was conventionally catalysed by palladium−phosphane complexes (Sonogashira, Tohda and Hagihara, 1975; Takahashi et al., 1980; Sonogashira, 2002). Their discovery engendered great interest since the products of this reaction are important intermediates in the synthesis of organic materials, pharmaceuticals and natural products (Sonogashira, Tohda and Hagihara, 1975; Takahashi et al., 1980; Sonogashira, 2002; Böhm and Herrmann, 2000; Cwik, Hell and Figueras, 2006; Hosseini-Sarvari, Razmi and Dorooodmand, 2014; Mujahidin and Doye, 2005; King and Yasuda, 2004). For example, the Sonogashira coupling procedure is used in the synthesis of the drug Terbinafine, which is used as an antifungal agent (Torborg and Beller, 2009; Beutler et al., 1996).

In most cases, the conventional Sonogashira coupling reactions are carried out under homogeneous conditions, which involve using palladium complexes such as [PdCl₂(PPh₃)₂] or [Pd(PPh₃)₄] (3−5 mol%), a catalytic amount of a Cu salt (3-10 mol%) and an amine in large excess (Sonogashira, Tohda and Hagihara, 1975; Sonogashira, 2002; Rosa et al., 2015; Ciriminna et al., 2013). The use of copper salts as co-catalysts accelerates the Sonogashira reaction greatly; however, their presence in the reaction yields alkyne dimers (Sisodiya et al., 2015). This leads to the generation of an undesired homocoupling product of the alkyne upon oxidation. Thus, the reaction must be conducted under inert atmosphere if a Cu salt is to be used as a co-catalyst (Sisodiya et al., 2015). Furthermore, the above-mentioned standard conditions require a high loading of palladium and involve the use of phosphine ligands that are usually oxygen-sensitive (Cwik, Hell and Figueras, 2006). In addition, the efficient separation and subsequent recycling of homogenous palladium catalysts and ligand remains a challenge and an aspect of environmental and economic relevance (Roy, Senapati and Phukan, 2015).

Intensive studies on heterogenization of Sonogashira coupling reactions with the objective of combining the benefits of both heterogeneous and homogeneous catalysis have been carried out during the last three decades (Abu-Reziq and Alper, 2012). In this direction, researchers have immobilised Pd on solid supports such as activated carbon (charcoal) (Rossy et al., 2014), zeolites Pd₀.₀₂Ce₀.₉₈O₂₋₈: a copper- and ligand-free quasi-heterogeneous catalyst for aquacatalytic Sonogashira cross-coupling reaction


Synopsis
A Pd₀.₀₂Ce₀.₉₈O₂₋₈ solid solution oxide was synthesised in one step using a urea-assisted solution combustion method. XRD, ICP-OES, BET, XPS, SEM, EDX, TEM, TGA and Raman spectroscopy were used to study the structural and electronic properties of the as-prepared Pd₀.₀₂Ce₀.₉₈O₂₋₈ catalyst. The catalyst testing results revealed that the Pd₀.₀₂Ce₀.₉₈O₂₋₈ system performs as an efficient precatalyst for the Sonogashira cross-coupling reactions under copper- and ligand-free conditions. A wide range of iodoarenes were efficiently coupled to phenylacetylene with good to excellent isolated yields. A thorough investigation through a series of suitable experiments explicitly showed that the Sonogashira cross-coupling reaction is accomplished via a quasi-heterogeneous mechanism by the leached Pd(0) species. As a result, the Pd₀.₀₂Ce₀.₉₈O₂₋₈ lost some activity upon recycling.

Keywords
Pd²⁺ substituted ceria, solution combustion, nanoparticles and Sonogashira coupling reactions.


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**Pd$_{0.02}$Ce$_{0.98}$O$_{2-\delta}$: a copper- and ligand-free quasi-heterogeneous catalyst**

(Djakovitch and Rollet, 2004), metal oxides (Cwik, Hell and Figueras, 2006; Hosseini-Sarvar, Razmi and Doroodmand, 2014; Roy, Senapati and Phukan, 2015; Kotadia et al., 2014) (MgO, ZnO, TiO$_2$, ZrO$_2$, Fe$_2$O$_3$, CeO$_2$, ...), clays (Borah and Dutta, 2013), alkaline earth salts (CaCO$_3$, BaSO$_4$, BaCO$_3$, SrCO$_3$) (Barros et al., 2008) and organic polymers (Ye and Yi, 2008; Kim et al., 2007). However, the leaching of palladium from the catalyst is still the main problem, even though most researchers have reported that their catalysts can be recycled by the redeposition of Pd onto the support (Redon, Peña and Crescencio, 2014). This is due to the quasi-heterogeneous mechanism of the Sonogashira cross-coupling reaction via the solvated palladium clusters (Reay and Fairlamb, 2015).

Hence, quasi-heterogeneous catalysis has developed into a new stream in catalysis and is a promising approach for bridging heterogeneous and homogeneous catalysis (Abu-Reziq and Alper, 2012). Quasi-heterogeneous catalysis relies on the fact that nano-supports have a large surface areas, thus they can retain the activity and selectivity of the supported catalysts (Abu-Reziq and Alper, 2012; Wu et al., 2011).

In this regard, we thought it would be worthwhile to develop a general catalytic system for a copper- and ligand-free quasi-heterogeneous Sonogashira coupling reaction catalysed by a nano Pd$_{0.02}$Ce$_{0.98}$O$_{2-\delta}$ solid solution oxide. To the best of our knowledge, Pd$_x$Ce$_{1-x}$O$_{2-\delta}$ based solid-solution oxides have not previously been investigated on the Sonogashira coupling reactions. Using an air, moisture and thermally stable quasi-heterogeneous Pd$_{0.02}$Ce$_{0.98}$O$_{2-\delta}$ solid solution oxide should offer higher activity, simplicity of workup, recyclability and minimisation of metallic waste.

### Results and discussion

The structural and electronic properties of the Pd$_{0.02}$Ce$_{0.98}$O$_{2-\delta}$ catalyst have been deduced earlier by X-ray diffraction (XRD), XPS, XANES, Raman spectroscopy, EXAFS and high-resolution transmission electron microscopy (HR-TEM) (Cwele et al., 2016). The characterisation results indicated that the prepared material was a solid solution oxide with a fluorite structure. The Rietveld refined XRD profile of the prepared catalyst and the XPS of the Pd(3d) are shown in Figure 1. The X-ray pattern corresponds to a monophasic Pd$_{0.02}$Ce$_{0.98}$O$_{2-\delta}$ solid-solution oxide with a fluorite structure as reported earlier (Cwele et al., 2016). The insert in Figure 1 shows the XPS of the Pd(3d). The binding energy of Pd(3d$_{5/2}$) and Pd(3d$_{3/2}$) at 337.5 and 342.5 eV respectively, confirm that Pd is in the +2 oxidation state.

The crystal size and the lattice strain were estimated employing Williamson-Hall (W-H) plots and Equation [1].

The SEM and TEM images of CeO$_2$ and Pd$_{0.02}$Ce$_{0.98}$O$_{2-\delta}$ samples have very similar morphology (Figure 2). In both samples, the particles are present in the form of different sized lumps or flakes with rounded shaped structures. These types of structures are generated due to the nature of the solution combustion synthesis method, where gases escape giving rise to porosity. The BET surface area of the Pd$_{0.02}$Ce$_{0.98}$O$_{2-\delta}$ sample was found to be 58 m$^2$/g (Table I). The catalytic performance of the as-prepared Pd$_{0.02}$Ce$_{0.98}$O$_{2-\delta}$ solid-solution precatalyst was evaluated in the Sonogashira coupling of phenylacetylene and various haloarenes and the results are listed in Table II.

Optimisation of reaction conditions was conducted in order to develop a general catalytic system for the copper- and ligand-free Pd$_{0.02}$Ce$_{0.98}$O$_{2-\delta}$ catalysed Sonogashira coupling reaction.
PdₐCe₀.₉₈O₂₋δ: a copper- and ligand-free quasi-heterogeneous catalyst

We first conducted investigations to find a solvent system that is conducive for the Sonogashira coupling reaction (Figure 4). The solvent systems investigated were: acetonitrile (CH₃CN), DMF, toluene (PhMe), ‘solvent-less’ and H₂O/CH₃CN (1:3 v/v). Toluene gave the lowest conversion of 32% after 8 hours, while ‘solvent-free’ and acetonitrile conditions gave relatively high conversion, of 68% and 80% respectively. DMF gave 100% conversion in 3 hours, while H₂O/acetonitrile (1:3 v/v) went to completion in an hour. Hence, further investigations were conducted in H₂O/acetonitrile (1:3 v/v). Böhm and Herrmann (2000) reported that the polarity and hydrogen bonding ability of the solvent are important in accelerating the reaction by stabilizing the ionic intermediates of the catalytic cycle. The solvent investigation results agree well with the above statement, since the reaction conducted in toluene has the longest reaction time and the lowest percentage conversion, while those conducted in aqueous acetonitrile had the shortest reaction time and gave 100% conversion of phenylacetylene. The Böhm and Herrmann findings also indirectly address the nature of catalysis for most Sonogashira coupling procedures (discussed later).

The choice of base is considered crucial in Sonogashira coupling reactions. The base is used to neutralise the acid (HX) formed as a by-product in this reaction (Böhm and Herrmann, 2000). In addition, the base plays a role in inhibiting the generation of a homo-coupling product (Glaser-type reaction) and its strength plays a key role in the deprotonation of terminal alkynes (Böhm and Herrmann, 2000).

Table I

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Lattice parameter a (Å)</th>
<th>Lattice strain (10⁻²)</th>
<th>Crystallite size (nm)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>5.4221</td>
<td>1.10</td>
<td>8</td>
<td>69</td>
</tr>
<tr>
<td>PdₐCe₀.₉₈O₂₋δ</td>
<td>5.4200</td>
<td>4.20</td>
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</tbody>
</table>

Table II

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Reaction time/h</th>
<th>Conversion/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ca₂CO₃</td>
<td>24</td>
<td>62</td>
</tr>
<tr>
<td>2</td>
<td>Et₃N</td>
<td>1</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>K₂CO₃</td>
<td>24</td>
<td>66</td>
</tr>
<tr>
<td>4</td>
<td>NaOAc</td>
<td>24</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td>NaOH</td>
<td>24</td>
<td>48</td>
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</tbody>
</table>

The choice of base is considered crucial in Sonogashira coupling reactions. The base is used to neutralise the acid (HX) formed as a by-product in this reaction (Böhm and Herrmann, 2000). In addition, the base plays a role in inhibiting the generation of a homo-coupling product (Glaser-type reaction) and its strength plays a key role in the deprotonation of terminal alkynes (Böhm and Herrmann, 2000).
Pd$_{0.02}$Ce$_{0.98}$O$_2$-5: a copper- and ligand-free quasi-heterogeneous catalyst

Among the investigated bases, triethylamine was found to be the best base under our reaction conditions (Table II). The reaction went to completion in just an hour when triethylamine was used as base, but did not go to completion with the other bases investigated ($\text{K}_2\text{CO}_3$, NaOH, CH$_3$COONa and Cs$_2$CO$_3$). It has been suggested that amines do not act as bases only, but also as weak coordinating ligands (Jutand, Négri and Principaud, 2005). Hence, beside the observed solubility problem when the inorganic bases were used, the fact that triethylamine can act as a coordinating base is thought to be a major reason for its superior performance.

Three different temperatures were also investigated; 25, 50 and 82°C (Figure 5). It was found that the reactions were most rapid under refluxing conditions (82°C).

Several experiments were conducted to find the lowest amount of the catalyst loading (based on Pd) that could efficiently catalyse the Sonogashira coupling reactions in reasonable reaction times (Figure 6). The investigations were initiated with catalyst loading between 0.05-1 mol%. For loadings of 0.1-1 mol%, the reaction was found to be very fast and the reaction went to completion in an hour. This fast reaction makes it difficult to monitor the substitution and electronic effect caused by the aryl halides. Hence, a catalyst loading of 0.05 mol% was investigated; this then gave a slower reaction that went to completion in 3 hours.

A combination of aryl halides and terminal alkynes was then studied to investigate the scope and limitations of our catalytic system under the obtained optimum reaction conditions. The investigations were initiated by reacting various iodoarenes with phenylacetylene, to investigate the electronic effect and the substitution position effect on the haloarenes.

It was found that the aryl halides with electron-withdrawing groups in the para-position (Table III, entries 4, 5, 9 and 11) react more rapidly compared to those with
electron-donating groups in the same position (Table III, entries 2, 3 and 7). Hence, the electronic effect dictates the catalyst activity in the Sonogashira coupling reactions. It was also noted that the position of each functional group on the aryl halide also controls the activity of the catalyst. This is best demonstrated by the reactivity of 4-iodotoluene and 3-iodotoluene (Table III, entries 7 and 8); where the 3-iodotoluene reacts three times faster than 4-iodotoluene. These findings agree well with the reported influence of substituents in aryl halides on Sonogashira coupling reactions (Sonogashira, Tohda and Hagihara, 1975; Takahashi et al., 1980; Sonogashira, 2002).

With the success obtained with aryl iodides, the reactions were extended to aryl bromides and aliphatic alkynes. However, bromoarenes, chloroarenes and aliphatic alkynes found to be unreactive under the obtained optimum conditions. The stability of the C−Cl and C-Br bonds makes chloroarenes and bromoarenes notoriously less reactive. Even under homogeneous copper-free coupling reaction conditions, aryl bromides give fairly low conversions (10-60%) (Cwik, Hell and Figueras, 2006).

Hence, the obtained optimum conditions are limited to iodoarenes and aromatic alkynes as coupling partners only. Performance comparisons of the present catalyst in Sonogashira cross coupling reactions of iodobenzene and phenylacetylene against other related Cu- and ligand-free catalytic systems are shown in Table IV.

**Leaching and recyclability test**

A strong test for evaluating heterogeneity of a catalyst is the hot filtration test. To determine whether the reactions reported here were homogeneous or heterogeneous, a hot filtration test was performed for the Sonogashira coupling of

| Table III |
| Sonogashira cross-coupling of phenylacetylene with various iodoarenes to give substituted biphenylacetylenes under our optimum reaction conditions |

<table>
<thead>
<tr>
<th>Entry</th>
<th>Iodoarene</th>
<th>Reaction time (h)</th>
<th>Isolated yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>3</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>4</td>
<td>94</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>44</td>
<td>70</td>
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<tr>
<td>4</td>
<td></td>
<td>2</td>
<td>91</td>
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<td>5</td>
<td></td>
<td>1</td>
<td>90</td>
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<tr>
<td>6</td>
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<td>1</td>
<td>93</td>
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<tr>
<td>12</td>
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<td>1</td>
<td>93</td>
</tr>
</tbody>
</table>

**Pd\textsubscript{0.02}Ce\textsubscript{0.98}O\textsubscript{2−δ}: a copper- and ligand-free quasi-heterogeneous catalyst**
Pd$_{0.02}$Ce$_{0.98}$O$_2$-$\delta$: a copper- and ligand-free quasi-heterogeneous catalyst

Phenylacetylene and iodobenzene. The catalyst was filtered off from the reaction mixture after 5 minutes and the hot filtrate was then allowed to react further under similar conditions. The reaction was then monitored every 15 minutes for 2 hours. Assessment of the rate of iodobenzene conversion from the fresh reaction and the hot filtration test suggests that the activity in the fresh reaction can be attributed to the Pd species in the solution (Figure 7). The fresh catalyst and the hot filtrate have almost identical reaction profiles (Figure 7). An ICP analysis of the filtered solution confirmed the presence of about 0.5 ppm of Pd in the hot filtrate.

Since the active catalytic phase was evidently the leached Pd, we attempted to determine the active Pd species using the mercury-poisoning test. Hg(0) is known to form amalgams with a variety of metals in their zero oxidation state (Reay and Fairlamb, 2015). Hence, if Pd dissociates from the solid Pd$_{0.02}$Ce$_{0.98}$O$_2$-$\delta$, it would bind with Hg(0) thereby quenching its catalytic activity. However, Pd in a raised oxidation state is not expected to be quenched by Hg(0) (Reay and Fairlamb, 2015). Thus, the mercury-poisoning test was used to establish whether bare Pd(0) did participate in catalysing the Sonogashira coupling reactions.

To do the mercury poison test for the system described here, the Pd$_{0.02}$Ce$_{0.98}$O$_2$-$\delta$ catalyst was filtered-off from the reaction mixture after a reaction time of 5 minutes and 2.5 mmol Hg(0) was added to the hot reaction mixture. The reaction mixture was then allowed to react further under similar conditions, while the activity was monitored every 15 minutes. It was found that no further reaction occurred after 15 minutes. Thus, the analysis confirms the presence of Pd(0) in the solution, which in turn gives insight into the reaction mechanism. Hence, the Pd$_{0.02}$Ce$_{0.98}$O$_2$-$\delta$-catalysed Sonogashira coupling reaction is essentially a quasi-heterogeneous catalytic process occurring over solvated Pd(0) clusters.

The recycled catalyst showed about 60% conversion of iodobenzene in 2 hours. Hence, the recyclability test suggests that some of the leached Pd can redeposit on the CeO$_2$ support at the end of the Sonogashira reaction and/or the Pd$_{0.02}$Ce$_{0.98}$O$_2$-$\delta$ serves as an active catalyst reservoir.

**Proposed mechanism**

The exact mechanism by which the quasi-heterogeneous Pd$_{0.02}$Ce$_{0.98}$O$_2$-$\delta$-catalysed copper- and ligand-free Sonogashira coupling reaction occurs is still under investigation. However, the catalytic activity results, leaching and recyclability tests seem to indicate that the reaction follows a Pd(0)/Pd(2+) mechanism (Scheme 2 – Figure 8). We proposed that the first step in the reaction mechanism is ‘pre-activation’ which allows Pd$_2$(0.02)Ce$_{0.98}$O$_2$-$\delta$ to enter the catalytic cycle as Pd$_0$/CeO$_2$. The Pd(2+) ions in the fresh catalyst are reduced *in situ* by triethylamine and/or the solvent system (H$_2$O/acetonitrile) to Pd(0). (Tougerti, Negri and Jutand, 2007; Jutand, Negri and Principaud, 2005) Since Pd(0) is more electron rich than Pd(2+), it allows for oxidative addition of the iodoarene, which marks the beginning of the catalytic cycle. The alkyne coordinates and forms a pi complex with Pd and then the desired Sonogashira coupling product is generated through the reductive elimination step.

**Conclusion**

In conclusion, we have developed a general and simple process for Sonogashira coupling reactions using...
**Pd$_{0.02}$Ce$_{0.98}$O$_{2-δ}$: a copper- and ligand-free quasi-heterogeneous catalyst**

Pd$_{0.02}$Ce$_{0.98}$O$_{2-δ}$ as a precatalyst. The catalyst was found to be very effective in a water/acetonitrile solvent system at 82°C under ligand- and Cu-free reaction conditions. A wide range of iodoarones were coupled to phenylacetylene using this catalytic route. It was also found that the Pd$_{0.02}$Ce$_{0.98}$O$_{2-δ}$ catalysed Sonogashira cross-coupling reactions are essentially a quasi-heterogeneous catalytic process occurring over solvated Pd(0) clusters. As a result, the recovered catalyst loses some activity upon recycle.

**Experimental section**

Cerium ammonium nitrate [(NH$_3$)$_2$Ce(NO$_3$)$_6$, 99.9%], palladium chloride [PdCl$_2$, 60%], urea [CH$_4$N$_2$O, 99.9%] were obtained from Sigma-Aldrich and were used without further purification.

**Procedure for synthesis of Pd$_{0.02}$Ce$_{0.98}$O$_{2-δ}$**

The monophasic Pd$_{0.02}$Ce$_{0.98}$O$_{2-δ}$ solid-solution oxide was prepared using a one-step urea-assisted solution combustion synthesis method described earlier (Cwele et al., 2016). The catalyst synthesis method involved preparation of a redox combustion mixture composed of stoichiometric amounts of metal precursors [(NH$_3$)$_2$Ce(NO$_3$)$_6$ and PdCl$_2$] and urea [NH$_2$CONH$_2$] in the ratio of 1.0:3.77 respectively, dissolved in water. The solution was then stirred at 150°C for 10 minutes to evaporate water and reduce its volume to approximately 20 mL. The boiling solution was then introduced into a muffle furnace pre-heated at 400°C and was kept in the furnace overnight. A light brown solid was obtained.

**Catalyst characterisation**

A Bruker D8 Advance diffractometer, equipped with a XRK900 in-situ cell and a Cu K$_\alpha$ source ($\lambda = 1.5406 \AA$) was used to record the powder X-ray diffraction patterns of the samples. The structures were refined by the Rietveld method using the Full Prof Suite-2000 program. The average crystallite size ($D$) and lattice strain ($\varepsilon$) of CeO$_2$ and Pd$_{0.02}$Ce$_{0.98}$O$_{2-δ}$ were estimated from the modified Rietveld method and Williamson-Hall (W-H) plots.

**ICP-OES** was performed using a Perkin Elmer optical emission spectrometer Optima 5300 DV. Standards (1000 ppm Ce and Pd) were purchased from Fluka.

Brunauer–Emmett–Teller (BET) surface area measurements were determined using a MicroMetrics TriStar 3000 porosimeter with N$_2$ as probe gas. About 0.4 g of each powder sample was degassed overnight at 200°C using a Micromeritics FlowPep 060 instrument prior to analysis.

SEM images were obtained with a JEOL JSM-6100 scanning electron microscope using a Bruker signal processing unit detector. The analysis was performed at random points along the surface of the catalyst. The samples were first mounted on aluminium stubs using double-sided carbon tape; they were then coated with gold using a Polaron E5100 coating unit.

For TEM analysis, the samples were viewed on a Joel JEM-1010 electron microscope. For high-resolution TEM (HR-TEM) and scanning electron microscopy (STEM) analysis, the samples were viewed on a Joel JEM-2100 electron microscope and the images captured were analysed using iTEM software. The powder samples were ultrasonically dispersed in ethanol and supported on a perforated carbon film mounted on a copper grid prior to analysis.

**Catalyst testing: General procedure for sonogashira coupling reactions**

A dry two-necked pear-shaped flask containing a stirrer bar, a condenser, 2 mL of H$_2$O and 6 mL of acetonitrile was charged with aryl halide (2.3 mmol), phenylacetylene (2 eq.), triethylamine (5 eq.) and catalyst Pd$_{0.02}$Ce$_{0.98}$O$_{2-δ}$ (0.05 mol% Pd). The reaction mixture was stirred and (usually) heated to 82°C and its progress was monitored by GC and GC-MS. The iodoarene conversion was used to estimate the catalytic activity, using biphenyl as an internal standard. After the reaction had gone to completion, the reaction mixture was filtered and the filtrate was extracted with ethyl acetate and brine. The organic layer was then evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel using


Pd$_{0.02}$Ce$_{0.98}$O$_2$: a copper- and ligand-free quasi-heterogeneous catalyst

EtOAc/hexane (8/2) as an eluent. The structure of the coupling product was confirmed by 1H and $^{13}$C NMR spectroscopy and the results were consistent with those reported in the literature for substituted biphenylacetylenes (Djakovitch and Rollet, 2004).

General procedure for catalyst recovery and recyclability

The catalyst used in the first run was separated by centrifugation, washed with 5 mL acetonitrile, dried at 60°C and reused as described for the fresh catalyst.

Acknowledgements

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References


