

# RECYCLABLE PALLADIUM CATALYST CLOTHS FOR CARBON-CARBON COUPLING REACTIONS

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## **ABSTRACT**

Low loading palladium catalyst cloths have been prepared by surface complexation of palladium(II) chloride with plasmachemical imidazole functionalised non-woven polypropylene cloth. For Sonogashira, Mizoroki-Heck, and Suzuki-Miyaura carbon-carbon coupling reactions in conjunction with environmentally friendly solvents, high product yields (54%, 82%, and 99% respectively) and selectivities (99%, 93%, and greater than 99% respectively) have been measured. These palladium catalyst cloths show low levels of metal leaching and can be recycled multiple times.

## **KEYWORDS**

Palladium catalysis; catalyst cloth; carbon-carbon coupling reaction; Sonogashira; Mizoroki-Heck; Suzuki-Miyaura

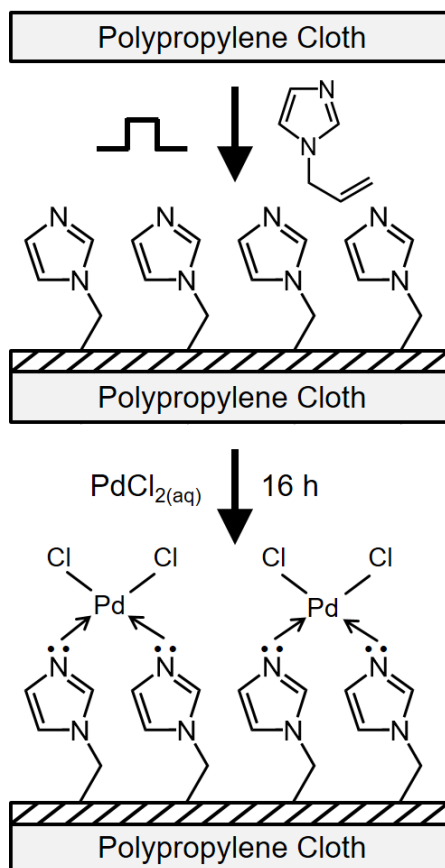
## 1 INTRODUCTION

Metal catalysed carbon-carbon coupling reactions are used in about 14% of all bulk organic synthesis good manufacturing processes (GMP);<sup>1</sup> with Sonogashira,<sup>2</sup> Mizoroki-Heck,<sup>3,4</sup> and Suzuki-Miyaura<sup>5</sup> variants being widely employed in the pharmaceutical industry.<sup>6</sup> Typically, homogeneous palladium catalysts are utilised but they can prove difficult to remove afterwards leading to problems with public health regulation compliance for metal contaminants in active pharmaceutical ingredients,<sup>7</sup> which leads to incurring additional costs associated with post-reaction metal capture steps. Furthermore, there is a strong drive towards making more use of environmentally friendly solvents during pharmaceutical production (such as ethanol-water mixtures).<sup>8,9,10</sup>

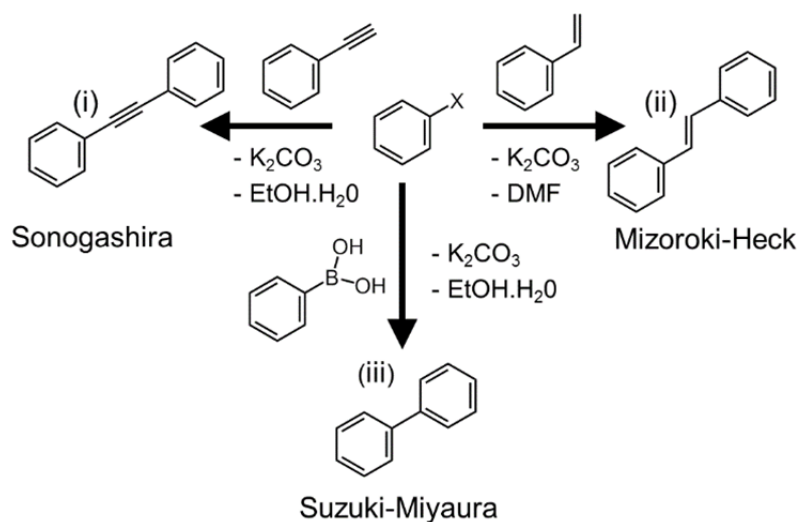
Heterogeneous (supported) catalysts can potentially address many of the aforementioned drawbacks associated with homogeneous palladium catalyst carbon-carbon coupling reactions. Existing commercially available materials include Pd/C, Pd/Al<sub>2</sub>O<sub>3</sub>, and loose polymer fibre anchored palladium(II) centres,<sup>11,12</sup> however these all require post-reaction filtration steps. There also exist dip catalysts for carbon-carbon coupling reactions (which do not require post-reaction filtration). For instance, palladium and nickel composite silica films dip coated onto glass supports rely on the sacrificial role of nickel, which ultimately limits the useable catalyst lifetime.<sup>13</sup> In the case of palladium nanoparticles supported on thin cellulose acetate polymer membranes, catalyst activity lasts only about 3 h.<sup>14</sup> Longer life catalysts have been reported for palladium nanoparticles incorporated into spin coated poly(vinyl alcohol);<sup>15</sup> however, these free standing multilayer films of just 1 µm thickness are difficult to handle for industrial scale processing. In the case of palladium nanoparticles incorporated onto cellulose paper and wool only 5–6 recycles are feasible,<sup>16,17</sup> whilst incorporation of palladium(II) species within a polymer film as an alternative to palladium nanoparticles suffers from high levels of metal leaching contributing towards homogeneous (rather than heterogeneous) catalysis.<sup>18,19,20,21</sup>

Although imidazole based ligands for palladium catalysis are extensively used in homogeneous Mizoroki-Heck<sup>22,25</sup> and Suzuki-Miyaura<sup>23,24,25,26</sup> coupling reactions, their application on solid surfaces to anchor palladium catalysts has not been previously reported. In this article, we describe the anchoring of palladium catalyst

sites through surface imidazole groups formed by pulsed plasma deposition of poly(1-allylimidazole) onto a cheap non-woven polypropylene support, Scheme 1. Pulsed plasma deposition comprises modulating an electrical discharge in the presence of gaseous precursors containing polymerizable carbon-carbon double bonds.<sup>27,28</sup> Mechanistically, there are two distinct reaction regimes corresponding to the plasma duty cycle on- and off- periods (typical timescales are of the order of microseconds and milliseconds respectively)<sup>29</sup>. Namely, monomer activation and reactive site generation at the substrate surface occur during each short burst of plasma (via VUV irradiation, ion, or electron bombardment) followed by conventional carbon-carbon double bond polymerization proceeding in the subsequent extended off-time (in the absence of any VUV-, ion-, or electron-induced damage to the growing film). High levels of precursor structural retention within the deposited nanolayer can be achieved, thereby yielding specific functionalities at the surface (as confirmed by ToF-SIMS<sup>30</sup> and NMR<sup>31</sup>). Furthermore, by programming the pulsed plasma duty cycle, it is possible to control (i.e. tailor) the surface density of desired chemical groups. The covalent attachment of the functional films to the underlying substrate occurs via free radical sites created at the interface during the onset of plasma exposure. Other distinct advantages include the fact that the plasmachemical approach is quick (single-step), solventless, energy-efficient, and the reactive gaseous nature of the electrical discharge provides conformality to a whole host of substrate materials and complex geometries (e.g. powders, fibres, tubes, cloths, etc.).<sup>32,33</sup> Surface functionalities devised in the past include: anhydride,<sup>29</sup> carboxylic acid,<sup>34</sup> amine,<sup>35</sup> cyano,<sup>36</sup> epoxide,<sup>30</sup> hydroxyl,<sup>37</sup> halide,<sup>38</sup> thiol,<sup>39</sup> furfuryl,<sup>40</sup> perfluoroalkyl,<sup>41</sup> perfluoromethylene,<sup>42</sup> and trifluoromethyl<sup>43</sup> groups. In the present study, palladium catalyst cloths prepared using surface imidazole groups have been evaluated for Sonogashira, Mizoroki-Heck, and Suzuki-Miyaura carbon-carbon coupling reactions, as well as recycling studies, Scheme 2.



Scheme 1: Pulsed plasmachemical deposition of poly(1-allylimidazole) onto polypropylene cloth followed by surface tethering of palladium catalyst species.



Scheme 2: Carbon-carbon coupling reactions of haloarene using palladium catalyst cloth: (i) Sonogashira coupling reaction with phenylacetylene; (ii) Mizoroki-Heck coupling reaction with styrene; and (iii) Suzuki-Miyaura coupling reaction with phenylboronic acid. Where X is a halogen atom.

## 2 EXPERIMENTAL SECTION

### 2.1 Pulsed Plasma Deposition of Poly(1-allylimidazole)

A cylindrical glass reactor (5.5 cm diameter, 475 cm<sup>3</sup> volume) housed within a Faraday cage was used for plasmachemical deposition. This was connected to a 30 L min<sup>-1</sup> rotary pump (E2M2, Edwards Vacuum Ltd.) via a liquid nitrogen cold trap (base pressure less than  $2 \times 10^{-3}$  mbar and air leak rate better than  $6 \times 10^{-9}$  mol s<sup>-1</sup>).<sup>44</sup> A copper coil wound around the reactor (4 mm diameter, 10 turns, located 10 cm downstream from the gas inlet) was connected to a 13.56 MHz radio frequency (RF) power supply via an L-C matching network. A signal generator (model TG503, Thurlby Thandar Instruments Ltd.) was used to trigger the RF power supply. Prior to film deposition, the whole apparatus was thoroughly scrubbed using detergent and hot water, rinsed with propan-2-ol (+99.5 wt%, Fisher Scientific UK Ltd.), oven dried at 423 K, and further cleaned using a 50 W continuous wave air plasma at 0.2 mbar for 30 min. Silicon substrate preparation comprised successive sonication in propan-2-ol and cyclohexane (+99.7 wt%, Sigma-Aldrich Co.) for 15 min prior to insertion into the centre of the chamber. Further cleaning entailed running a 50 W continuous wave air plasma at 0.2 mbar for 30 min prior to film deposition. Non-woven polypropylene cloth (middle layer of disposable surgical face masks, SDMedical50pk, Security Direct, PO Box 1269) was used as provided. 1-allylimidazole (97 wt%, Acros Organics b.v.b.a.) precursor was loaded into a sealable glass tube, degassed via several freeze-pump-thaw cycles, and then attached to the reactor. Monomer vapour was then allowed to purge the apparatus at a pressure of 0.15 mbar for 15 min prior to electrical discharge ignition. Pulsed plasma deposition was performed using a duty cycle on-period ( $t_{on}$ ) of 20  $\mu$ s and a duty cycle off-period ( $t_{off}$ ) of 1200  $\mu$ s in conjunction with a RF generator power output ( $P_{on}$ ) of 30 W.<sup>45</sup> Upon plasma extinction, the precursor vapour was allowed to continue to pass through the system for a further 15 min, and then the chamber was evacuated to base pressure followed by venting to atmosphere. The equivalent of  $1.69 \pm 0.09$   $\mu$ m pulsed plasma deposition onto silicon wafers either side of the much higher surface area non-woven polypropylene material was sufficient to ensure that all the individual cloth fibres had a conformal coating (as confirmed by XPS which corresponds to a fibre coating thickness at least of the order of nanometres).

## 2.2 Surface Tethering of Pd Catalyst

The pulsed plasma deposited poly(1-allylimidazole) surfaces were immersed for 16 h into an aqueous catalyst solution comprising 2 mM palladium(II) chloride (+99.999 wt%, Alfa Aesar Co. Ltd.), 3.0 M sodium chloride (+99.5 wt%, Sigma-Aldrich Co.), and 0.5 M sodium citrate dihydrate (+99 wt%, Sigma-Aldrich Co.) in high purity water (BS 3978 Grade 1) adjusted to pH 4.5 with citric acid monohydrate (+99 wt%, Sigma-Aldrich Co.)<sup>46</sup>. The surfaces were then rinsed in high purity water for 20 min.

## 2.3 Film Characterization

Reflection-absorption infrared (RAIRS) spectra of pulsed plasma poly(1-allylimidazole) deposited onto silicon wafers were acquired using a FTIR spectrometer (Spectrum One, Perkin-Elmer Inc.) fitted with a liquid nitrogen cooled MCT detector operating at 4 cm<sup>-1</sup> resolution across the 400–4000 cm<sup>-1</sup> range. The instrument included a variable angle reflection-absorption accessory (Specac Ltd.) set to a grazing angle of 66° for silicon wafer substrates and adjusted for p-polarization. Attenuated total reflectance (ATR) infrared spectra of 1-allylimidazole precursor were obtained using a Golden Gate accessory (Specac Ltd.)

Film thickness values of pulsed plasma poly(1-allylimidazole) deposited onto silicon wafers were measured using a spectrophotometer (nkd-6000, Aquila Instruments Ltd.). Transmittance-reflectance curves (350–1000 nm wavelength range) were acquired for each sample and fitted to a Cauchy model for dielectric materials<sup>47</sup> using a modified Levenberg-Marquardt algorithm.<sup>48</sup> This was used to check for uniform deposition rate onto the non-woven polypropylene cloth material.

Surface elemental compositions of pulsed plasma poly(1-allylimidazole) deposited onto silicon wafers and non-woven polypropylene cloth were measured by X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB II electron spectrometer equipped with a non-monochromated Mg K $\alpha_{1,2}$  X-ray source (1253.6 eV) and a concentric hemispherical analyser. Photoemitted electrons were collected at a take-off angle of 20° from the substrate normal, with electron detection in the constant analyser energy mode (CAE, pass energies of 20 and 50 eV for high resolution and survey spectra respectively). Experimentally determined instrument sensitivity factors were C(1s) : O(1s) : N(1s) : Cl(2p) : Pd(3d) equals 1.00 : 0.35 :

0.70 : 0.37 : 0.06 respectively. The core level binding energy envelopes were fitted using a Gaussian peak shape and a linear background.<sup>49,50</sup> All binding energies were referenced to the C(1s) -C<sub>x</sub>H<sub>y</sub> hydrocarbon peak at 285.0 eV.<sup>51</sup>

## 2.4 Catalyst Testing and Product Analysis

Standard catalyst testing and product analysis procedures were followed (see Supplementary Material section).

## 2.5 Palladium Catalyst Loading

Palladium loading on the catalyst cloth, and amount leached during recycling studies was measured by ICP-OES (Vista MPX CCD Simultaneous axial ICP-OES, Varian Inc.). Calibration of detected palladium signal intensity to actual palladium content in solution was carried out to an accuracy of 0.01 ppm using reference samples at 1, 2, and 5 ppm, prepared from a 1000 ppm stock solution (26 X 1-Pd(a), MBH Analytical Ltd.) diluted in high purity water (resistance of 18.2 MΩ). Analyte solutions and palladium catalytic cloths were digested in 5 mL of sulphuric and perchloric acids (95 wt% Normapur®, and 65 wt% Normatom® respectively, VWR International Ltd.) by a wet ashing method followed by dilution to 25 mL in high purity water. The detection limit of palladium in these catalysis experiment analyte solutions was 0.1 ppm on a mass basis.

# 3 RESULTS

## 3.1 Surface Tethering of Palladium Catalyst

Infrared spectroscopy of pulsed plasma deposited poly(1-allylimidazole) films confirmed a high level of imidazole functional group structural retention,<sup>45</sup> Figure 1. Characteristic imidazole ring absorbances include: C=C–H ring stretch (3107 cm<sup>-1</sup>), C=N ring stretch (1504 cm<sup>-1</sup>), and N=C–H ring in-plane bend vibration (1107 cm<sup>-1</sup>).<sup>52</sup> Bands present in the 1560–1700 cm<sup>-1</sup> range can be attributed to a low level of plasma fragmented imidazole group C=N stretches,<sup>53</sup> and carbonyl stretches from adducts formed through atmospheric carbon dioxide adsorption.<sup>54,55</sup> Disappearance of the monoalkyl vinyl CH<sub>2</sub> wag (906 cm<sup>-1</sup>) associated with the precursor molecule



confirmed selective polymerisation of the vinyl group during pulsed plasma deposition.<sup>56</sup>

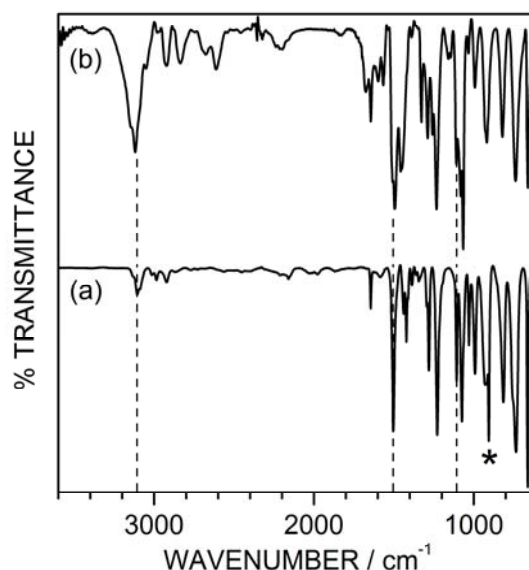


Figure 1: (a) ATR infrared spectra of 1-allylimidazole liquid precursor; and (b) RAIRS infrared spectra of pulsed plasma deposited poly(1-allylimidazole) ( $t_{on} = 20 \mu s$ ,  $t_{off} = 1200 \mu s$ ,  $P_{on} = 30 W$ , thickness =  $1.69 \pm 0.09 \mu m$ ). Dashed lines denote characteristic imidazole ring absorbances at  $3107 \text{ cm}^{-1}$ ,  $1504 \text{ cm}^{-1}$ , and  $1107 \text{ cm}^{-1}$ . \* Denotes monoalkyl vinyl  $\text{CH}_2$  wag at  $906 \text{ cm}^{-1}$ . Overall relative intensity differences between the two spectra are due to the use of ATR versus RAIRS infrared spectroscopy techniques.

XPS analysis of pulsed plasma deposited poly(1-allylimidazole) onto non-woven polypropylene cloth detected carbon, nitrogen, and a small amount of oxygen, Figure 2 and Table 1. The N(1s) binding envelope could be fitted to two different nitrogen environments at 398.7 eV and 400.5 eV, corresponding to the imidazole ring  $\text{C}=\underline{\text{N}}$  and  $\text{C}-\underline{\text{N}}$  nitrogen centres respectively,<sup>57</sup> Figure 3. Their slight deviation away from the theoretical 1 : 1 peak area ratio stems from a small amount of precursor fragmentation within the electrical discharge.<sup>53</sup> Immersing the imidazole functionalised cloth into aqueous palladium(II) chloride followed by rinsing in water gave rise to the appearance of palladium and chlorine XPS signals, signifying surface complex formation, Figure 2 and Scheme 1. This was accompanied by the relative attenuation in the 398.7 eV  $\text{C}=\underline{\text{N}}$  environment, which is consistent with metal complexation to imidazole ligand  $\text{C}=\underline{\text{N}}$  centres entailing nitrogen lone pair donation to the positively charged metal centre causing a decrease in electron density around the complexing nitrogen atom (increase in N(1s) XPS binding energy<sup>46,58</sup>), Figure 3. The detection of some oxygen signal can be attributed to factors such as water

absorption<sup>53</sup> and the formation of adducts through atmospheric carbon dioxide adsorption<sup>54,55</sup>.

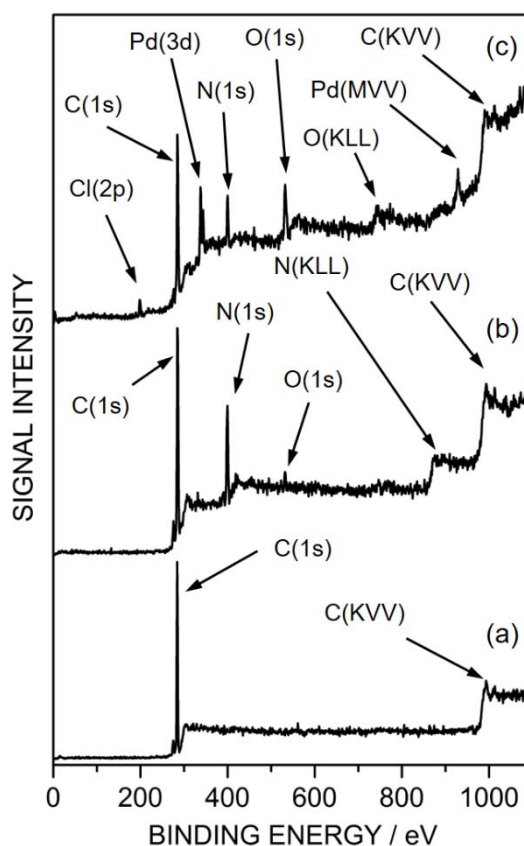


Figure 2: Wide scan XPS spectra of: (a) untreated polypropylene cloth; (b) pulsed plasma poly(1-allylimidazole) deposited onto polypropylene cloth ( $t_{on} = 20 \mu s$ ,  $t_{off} = 1200 \mu s$ ,  $P_{on} = 30 W$ ); and (c) following palladium(II) chloride complexation to imidazole functionalised cloth.

Table 1: XPS elemental relative atomic compositions at each stage of palladium catalyst cloth preparation and for a control sample in which polypropylene cloth without pulsed plasma poly(1-allylimidazole) functionalization was exposed to PdCl<sub>2</sub> solution.

Sample	C / %	N / %	O / %	Pd / %	Cl / %
Polypropylene cloth	100	-	-	-	-
Control polypropylene cloth exposed to palladium(II) chloride solution	93	-	7	-	-
Pulsed plasma poly(1-allylimidazole) coated polypropylene cloth	74 ± 1	24 ± 1	3 ± 1	-	-
Palladium catalyst cloth	64 ± 5	13 ± 2	16 ± 4	2 ± 1	5 ± 2

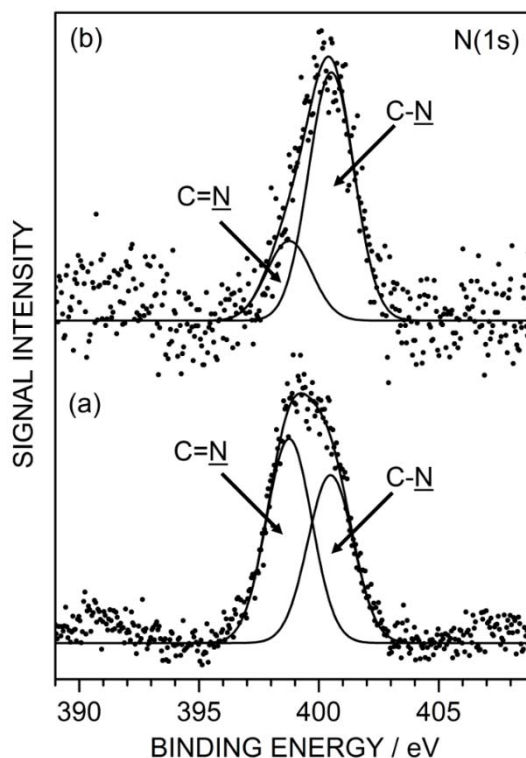
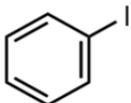
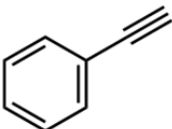


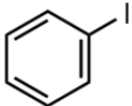
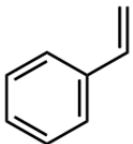
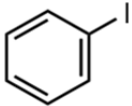
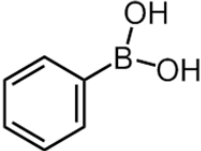
Figure 3: N(1s) XPS spectra: (a) pulsed plasma poly(1-allylimidazole) deposited onto polypropylene cloth ( $t_{on} = 20 \mu s$ ,  $t_{off} = 1200 \mu s$ ,  $P_{on} = 30 W$ ); and (b) following palladium(II) chloride complexation to cloth.

### 3.2 Palladium Cloth Catalysis

The prepared low loading (0.68 wt. %) palladium catalyst cloths were found to give very good product yields and high selectivities for Sonogashira, Mizoroki-Heck, and Suzuki-Miyaura coupling reactions of iodobenzene, Table 2.

Table 2: Cross-coupling reactions for iodobenzene ( $0.50 \pm 0.05$  mmol, stirred) using  $0.50 \pm 0.17 \mu mol$  palladium(II) catalyst cloths ( $7.9 \pm 2.6$  mg catalyst cloth with 0.68 wt% palladium loading), Scheme 2. Turn over frequency (TOF) is defined as the number of moles of product per mole of palladium per second,<sup>59</sup> assuming each palladium atom is an active site.

Coupling Reaction	Reagent 1	Reagent 2	Conditions	Yield / %	Selectivity / %	TOF / $h^{-1}$
Sonogashira		+ 	Ethanol-water, 12 h, 343 K	$54 \pm 3$	$99 \pm 1$	$45 \pm 2$

Mizoroki- Heck		+		Acetonitrile, 0.5 h, 413 K	$82 \pm 7$	$93 \pm 1$	$1640 \pm 131$
Suzuki- Miyaura		+		Ethanol- water, 0.5 h, 343 K	$99 \pm 1$	>99	$1980 \pm 20$

The Suzuki-Miyaura coupling reaction was further investigated by running a control experiment using 4-methoxyiodobenzene as a reactant with phenylboronic acid under similar reaction conditions in order to rule out the possibility of homocoupled by-product formation (GC-MS analysis of the resulting products showed the presence of only 4-methoxybiphenyl and biphenyl was not observed).

### 3.3 Recycling of Palladium Catalyst Cloth

Any possibility of palladium leaching from the catalyst cloths leading to predominantly homogeneous catalysis was checked by ICP-OES of the solution phase over 16 Suzuki-Miyaura and Sonogashira reaction cycles (i.e. 15 repeat cycles) in tandem with measurement of product yields, Figure 4 and Figure 5. Lower initial product yields were observed for both Suzuki-Miyaura and Sonogashira reactions during recycling studies when compared to single use studies, Table 2, this was due to the absence of stirring in the former case. The Suzuki-Miyaura coupling reaction for iodobenzene reactant showed minimal leaching ( $1.3 \pm 0.4\%$  per cycle of the starting 0.68 wt% palladium cloth loading). The observed decreasing trend in activity rules out purely homogeneous catalytic behaviour because the very low palladium leaching rate remains steady throughout the recycling studies.

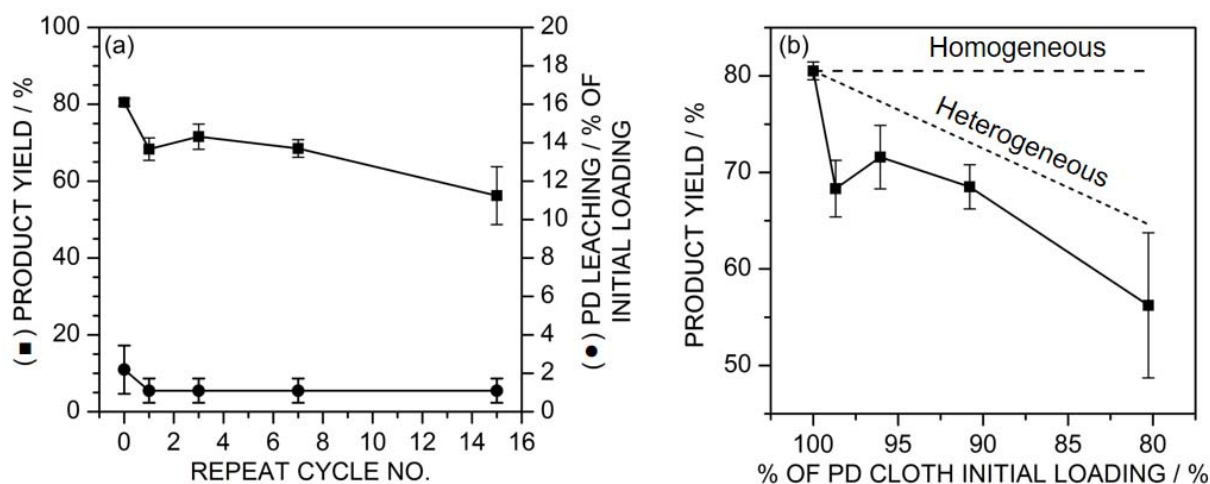


Figure 4: Recycling Suzuki-Miyaura coupling reaction of iodobenzene ( $0.50 \pm 0.05$  mmol iodobenzene, 343 K, 0.5 h per reaction, unstirred) using the same palladium catalyst cloth ( $7.9 \pm 2.6$  mg catalyst cloth, with  $0.50 \pm 0.17$   $\mu\text{mol}$  palladium(II) or 0.68 wt% initial palladium loading as measured by ICP-OES): (a) percentage product yield (■) and percentage palladium leaching of initial cloth loading per cycle (●) as a function of repeat cycle number; (b) percentage product yield as a function of the palladium loading remaining on the cloth (■) (calculated from the measured constant absolute value of palladium leaching per cycle of  $1.3 \pm 0.4\%$  of the starting cloth loading i.e. repeat cycle no. 0). Dashed lines represent theoretical product yields for exclusively homogeneous and heterogeneous palladium catalyst reaction pathways.

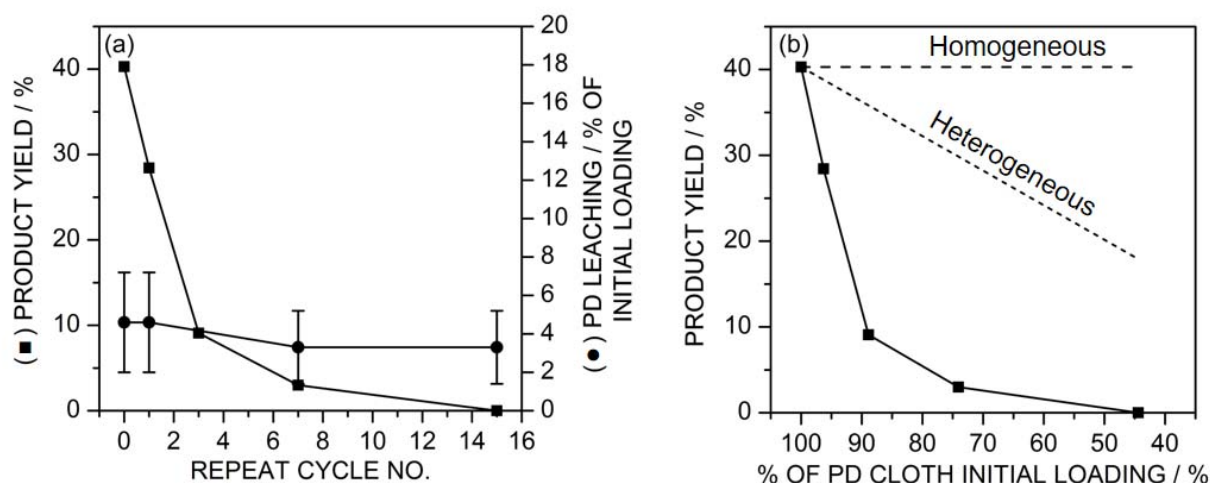


Figure 5: Recycling Sonogashira coupling reaction of iodobenzene ( $0.50 \pm 0.05$  mmol iodobenzene, 343 K, 12 h per reaction, unstirred) using the same palladium catalyst cloth ( $5.8 \pm 0.5$  mg catalyst cloth, with  $0.11 \pm 0.01$   $\mu\text{mol}$  palladium(II) or 0.21 wt% initial palladium loading as measured by ICP-OES): (a) percentage product yield (■) and percentage palladium leaching of initial cloth loading per cycle (●) as a function of repeat cycle number; (b) percentage product yield as a function of the palladium loading remaining on the cloth (■) (calculated from the measured constant absolute value of palladium leaching per cycle of  $3.7 \pm 1.1\%$  of the starting cloth loading i.e. repeat cycle no. = 0). Dashed lines represent theoretical product yields for exclusively homogeneous and heterogeneous palladium catalyst reaction pathways.

The aforementioned palladium cloth recycling trend observed for the Suzuki-Miyaura coupling reaction was confirmed for Sonogashira reactions over a much longer time period by lowering the catalyst loading on the cloth (0.21 wt% initial palladium loading equivalent to  $0.11 \pm 0.01 \mu\text{mol}$ ) and extending the reaction time (12 h per reaction) so as to allow monitoring over the full catalyst lifetime. The level of palladium leaching from the catalyst cloths remained low at  $3.7 \pm 1.1\%$  of starting cloth palladium loading (i.e. repeat cycle no. 0) per 12 h cycle throughout the overall Sonogashira reaction operational time of 192 h, at which point the cloth reached complete exhaustion, Figure 5. Again, the low level of palladium leaching remains steady in absolute terms, which rules out exclusive homogeneous palladium catalysis due to metal leaching because the product yield does not remain constant between consecutive recycles. Furthermore, the non-linearity of product yield with remaining palladium cloth loading suggests that either aggregation of metal atoms to form less active palladium clusters or poisoning is occurring on the cloth surface, Figure 5.

#### 4 DISCUSSION

Pulsed plasmachemical functionalisation of solid surfaces using polymerisable functional precursors is a well-established solventless, single-step, conformal, and substrate-independent technique, which offers the advantage of high levels of functional group retention,<sup>60</sup> thus making it well-suited for the preparation of cloth supported heterogeneous catalysts. Infrared and XPS analyses have shown that there is high level of imidazole ring retention during pulsed plasma deposition of 1-allylimidazole precursor, thereby facilitating palladium(II) ion complexation onto the surface, Scheme 1, Figure 1, and Table 1. The analogous  $[\text{Pd}(\text{allylimidazole})_2\text{Cl}_2]$  compound is reported to be stable at room temperature.<sup>61</sup> XPS analysis has shown that the measured N : Pd : Cl ratio of 6.5 : 1 : 2.5 is consistent with the formation of surface tethered  $[\text{Pd}(\text{im})_2\text{Cl}_2]$ , with the excess nitrogen content most likely arising from a combination of uncoordinated imidazole rings and a small degree of imidazole ring fragmentation during the pulsed plasma deposition process.<sup>53</sup>

Sonogashira, Mizoroki-Heck, and Suzuki-Miyaura coupling reactions of iodobenzene have demonstrated the practical viability of these palladium catalyst cloths. The palladium cloth loadings used for the Suzuki-Miyaura coupling reaction

(for the reaction solution equivalent to  $0.10 \pm 0.04$  mol% or  $18 \pm 6$  ppm on a mass basis) are lower than most previously reported dip catalysts (which range from 0.2 mol % to 2.0 mol%,<sup>13,14,16,17</sup> with a single instance of 0.06 mol%)<sup>15</sup> and are comparable to many dispersed solid supported heterogeneous catalysts.<sup>62,63,64,65,66,67,68,69</sup> Low palladium loading and high product yields for the Suzuki-Miyaura coupling of iodobenzene equates to a TOF of  $1980 \pm 20$  h<sup>-1</sup> (TON =  $990 \pm 10$ ), which surpasses the TOFs reported for all but one palladium dip catalyst (TOF =  $5808$  h<sup>-1</sup>);<sup>16</sup> however, the higher reaction temperatures and shorter reaction times used in that example (403 K and 5 min, compared to present 343 K and 30 min) are conducive to higher TOFs. Whilst very high TOFs of up to  $10^7$  h<sup>-1</sup> are achievable with dispersed solid supported palladium catalysts and homogeneous catalysts in both organic solvents and water, such catalysts require post reaction separation.<sup>62,70,71,72</sup>

The robustness of the catalyst cloths towards palladium leaching has been exemplified by following Sonogashira coupling over extended reaction times lasting days (choosing the lower than 99% reaction yield provided a meaningful check on monitoring yield changes). Palladium leaching over the total 192 h of catalyst cloth use was found to be less than  $3.3 \pm 0.7$  ppb h<sup>-1</sup> cm<sup>-3</sup> when using an initial cloth equivalent reaction solution loading of  $4.0 \pm 0.4$  ppm (on a mass basis or  $0.022 \pm 0.003$  mol%), thereby demonstrating the prolonged stability of the palladium catalyst cloth. This compares favourably with previously reported studies where the palladium catalyst leaching rate ranges from less than  $1$  ppb h<sup>-1</sup> cm<sup>-3</sup> to over  $100$  ppb h<sup>-1</sup> cm<sup>-3</sup>.<sup>15,62,64,65,67,68,73</sup> The observed drop in product yield with extended reaction time may be due to aggregation of palladium,<sup>74</sup> or catalyst poisoning. No breakdown point (characterised by a large rise in palladium leaching) was observed, highlighting the scope for far better reusability compared to existing state-of-the-art Fibrecat<sup>®</sup> commercial catalysts (which typically release increasing amounts of palladium after just three catalytic cycles<sup>12</sup>). The absence of any correlation between product yield and palladium leaching rules out the possibility of leached palladium species being primarily responsible for the observed catalysis, Figure 5.

Compared to conventional dispersed solid supported palladium catalysts which require post-reaction filtration or complicated chemical synthesis in the case of magnetic separation, the envisaged benefits for the use of such cloth catalysts

includes scope for environmentally friendly solvents, lower costs, ease of use, and recyclability.<sup>12,62,63,64,65,66,67,68,69,75</sup>

## **5 CONCLUSIONS**

Plasmachemical surface functionalisation with imidazole groups offers a cheap and quick approach for preparing low loading palladium catalyst cloths. These have been evaluated for Sonogashira, Mizoroki-Heck, and Suzuki-Miyaura carbon-carbon coupling reactions, and shown to exhibit high product yields (54%, 82%, and 99% respectively) and selectivities (99%, 93%, and greater than 99% respectively), whilst retaining catalytic activity over extended periods of usage (including recycling).

## **6 ACKNOWLEDGEMENTS**

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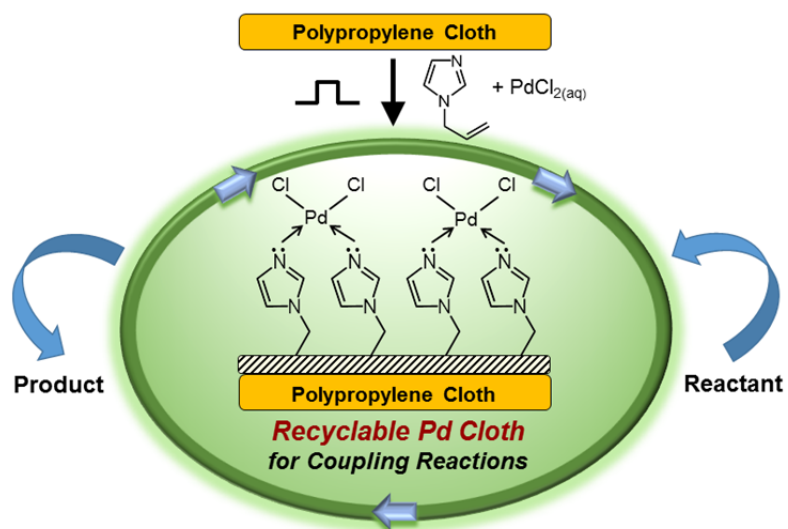
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## 8 GRAPHICAL ABSTRACT



## 9 HIGHLIGHTS

- Low loading palladium catalyst cloths.
- Carbon-carbon catalytic coupling reactions in environmentally friendly solvents.
- Minimal levels of catalyst leaching and recyclable.

# RECYCLABLE PALLADIUM CATALYST CLOTHS FOR CARBON-CARBON COUPLING REACTIONS

## (Supplementary Material)

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## 1 EXPERIMENTAL SECTION

### 1.1 Catalyst Testing

#### 1.1.1 *Sonogashira Coupling Reaction*

For single use palladium cloth studies, new B14 borosilicate sample flasks were thoroughly scrubbed using detergent and hot water, rinsed with acetone and oven dried at 373 K for 12 h. This cleaning procedure was followed before every reaction in order to remove any impurity. For single run studies on the palladium catalyst cloth ( $7.9 \pm 2.6$  mg catalyst cloth, with  $0.50 \pm 0.17$   $\mu\text{mol}$  of palladium(II) or 0.68 wt% ( $53.7 \pm 17.9$   $\mu\text{g}$ ) initial palladium loading as measured by ICP-OES analysis). The B14 flask was fitted to a B14 water cooled condenser, and immersed in a water bath at 343 K for 12 h for the reaction to proceed using a PTFE coated stirrer bar agitated at 500 rpm. Afterwards, the flask was removed from the water bath and allowed to cool to room temperature, after which the catalyst cloth was removed and the solution decanted. The flask was then rinsed twice with 2.5 mL of chloroform (99.8 wt%, Merck KGaA) and the washings were added to the decanted solution. The combined solution was washed twice with 3 mL of water, and the organic portion was dried over anhydrous sodium sulphate (99 wt%, SD-Fine Chem Ltd.) before analysis by GC and GC-MS without further dilution.

In the case of palladium cloth recycling studies, B10 borosilicate sample flasks (Scientific Glass Laboratories Ltd.)<sup>1</sup> were rinsed with ethanol (+99.8 wt%, Fisher Scientific UK Ltd.), thoroughly scrubbed using detergent and hot water, followed by immersion for 10 h in a solution comprising sodium hydroxide (99.2 wt%, Fisher Scientific UK Ltd.), propan-2-ol, and high purity water in a mass ratio 1 : 20 : 5 in order to remove any organic residue. The flasks were then thoroughly scrubbed using detergent and hot water, rinsed in propan-2-ol, and oven dried at 423 K. A final wash step consisted of immersion for 1 h in a 1 wt% nitric acid bath (70 wt% in water, Fisher Scientific UK Ltd., further diluted in high purity water), followed by thorough rinsing with high purity water and oven drying at 423 K, to ensure that no palladium transfer occurred between solutions. This rigorous cleaning procedure was undertaken before each reaction.  $0.50 \pm 0.01$  mmol of iodobenzene (98 wt%, Sigma-Aldrich Co.),  $0.74 \pm 0.01$  mmol of phenylacetylene (98 wt%, Sigma-Aldrich

Co.), and  $0.99 \pm 0.01$  mmol of  $K_2CO_3$  (98 wt%, Sigma-Aldrich Co.) were weighed out into a borosilicate flask. 3 mL of a solution comprising ethanol and high purity water in a 2 : 1 volume ratio was added, the flask was agitated to dissolve the  $K_2CO_3$ , and then the catalyst cloth was added ( $5.8 \pm 0.5$  mg catalyst cloth, with  $0.11 \pm 0.01$   $\mu$ mol palladium(II) or 0.21 wt% ( $12 \pm 1$   $\mu$ g) initial palladium loading as measured by ICP-OES analysis (Vista MPX, Varian Inc.)). The B10 flask was fitted to a B10 water cooled condenser, and immersed in a water bath at 343 K for 12 h for the reaction to proceed. For these recycling studies, the stirrer was not included in order to prevent abrasive damage to the cloth material over sequential recycling runs. Afterwards, the flask was removed from the water bath and allowed to cool to room temperature, after which the catalyst cloth was removed and the solution decanted. The flask was then rinsed twice with 1 mL of chloroform (99.8 wt%, Fisher Scientific UK Ltd.) and the washings were added to the decanted solution. Solutions for GC analysis were extracted three times with 3 mL of chloroform, spiked with 4 mg  $ml^{-1}$  decane (0.1 g, +99 wt%, Sigma-Aldrich Co.), and made up to 25 mL with dichloromethane (99.99 wt%, Fisher Scientific UK Ltd.). Solutions for ICP-OES analysis were sealed in screw topped borosilicate glass vials fitted with a PTFE/silicone slit septum (J.G Finneran Associates Inc. part no. 603570-08). The catalyst cloths were dried in air at 293 K for a minimum of 1 h before reuse in recycling studies with a fresh reactant solution each time.

### **1.1.2 Mizoroki-Heck Coupling Reaction**

A PTFE lined autoclave 15 mL was thoroughly scrubbed using detergent and hot water, rinsed with acetone and oven dried at 373 K for 12 h. This cleaning procedure was followed before every reaction.  $0.50 \pm 0.01$  mmol of iodobenzene (98 wt%, Sigma-Aldrich Co.),  $0.75 \pm 0.01$  mmol of styrene (99 wt%, Sigma-Aldrich Co.), and  $0.99 \pm 0.005$  mmol of  $K_2CO_3$  (98 wt%, Loba Chemie Pvt. Ltd.) were weighed out into a PTFE lined autoclave. 3 mL of acetonitrile (99.8 wt%, S D Fine-Chem Ltd.) was added, the autoclave was agitated and the catalyst cloth was added ( $7.9 \pm 2.6$  mg catalyst cloth, with  $0.50 \pm 0.17$   $\mu$ mol of palladium(II) or 0.68 wt% ( $53.7 \pm 17.9$   $\mu$ g) initial palladium loading as measured by ICP-OES analysis). The autoclave was fitted with a PTFE coated magnetic stirrer, agitated at 500 rpm, and heated to 413 K for 6 h for the reaction to proceed. Afterwards, the autoclave was left to cool to room

temperature, after which the catalyst was removed and the solution decanted. The autoclave was rinsed twice with 1 mL of acetonitrile and twice with 1 mL of ethyl acetate (99.5 wt%, S D Fine-Chem Ltd). The washings were added to the decanted solution before analysis by GC and GC-MS without further dilution.

### **1.1.3 Suzuki-Miyaura Coupling Reaction**

For single use palladium cloth studies, new B14 borosilicate sample flasks were thoroughly scrubbed using detergent and hot water, rinsed with acetone and oven dried at 373 K for 12 h. This cleaning procedure was followed before every reaction. The B14 flask was fitted to a B14 water cooled condenser, and immersed in a water bath at 343 K for 30 min for the reaction to proceed using a PTFE coated stirrer bar agitated at 500 rpm. Afterwards, the flask was removed from the water bath and allowed to cool to room temperature, after which the catalyst cloth was removed and the solution decanted. The flask was then rinsed twice with 2.5 mL of chloroform and the washings were added to the decanted solution. The combined solution was washed twice with 3 mL of water, and the organic portion was dried over anhydrous sodium sulphate before analysis by GC and GC-MS without further dilution.

In the case of palladium cloth recycling studies, B10 borosilicate sample flasks were rinsed with ethanol, thoroughly scrubbed using detergent and hot water, followed by immersion for 1 h in a solution comprising sodium hydroxide, propan-2-ol, and high purity water in a mass ratio 1 : 20 : 5 in order to remove any organic residue. The flasks were then thoroughly scrubbed using detergent and hot water, rinsed in propan-2-ol, and oven dried at 423 K. A final wash step consisted of immersion for 1 h in a 1 wt% nitric acid bath, followed by thorough rinsing with high purity water and oven drying at 423 K, to ensure that no palladium transfer occurred between solutions. This rigorous cleaning procedure was undertaken before each reaction.  $0.50 \pm 0.05$  mmol of iodobenzene,  $0.75 \pm 0.01$  mmol of phenylboronic acid, and  $0.99 \pm 0.01$  mmol of  $K_2CO_3$  were weighed out into a borosilicate flask. 3 mL of a solution comprising ethanol and high purity water in a 2 : 1 volume ratio was added, the flask was agitated to dissolve the  $K_2CO_3$ , and then the catalyst cloth was added ( $7.9 \pm 2.6$  mg catalyst cloth, with  $0.50 \pm 0.17$   $\mu$ mol of palladium(II) or 0.68 wt% ( $53.7 \pm 17.9$   $\mu$ g) initial palladium loading as measured by ICP-OES analysis). Alternatively,  $0.50 \pm 0.05$  mmol of 4-methoxyiodobenze (98 wt%, Sigma-Aldrich Co.) was

substituted for iodobenzene to rule out homocoupled by-product formation. The flask was fitted to a water cooled condenser, and immersed in a water bath at 343 K for 30 min for the reaction to proceed. For these recycling studies, the stirrer was not included in order to prevent abrasive damage to the cloth material over sequential recycling runs. Afterwards, the flask was removed from the water bath and allowed to cool to room temperature, after which the catalyst cloth was removed and the solution decanted. The flask was then rinsed twice with 1 mL of chloroform and the washings were added to the decanted solution. Solutions for GC analysis were extracted three times with 3 mL of chloroform, spiked with 4 mg ml<sup>-1</sup> decane (0.1 g), and made up to 25 mL with dichloromethane. Solutions for ICP-OES analysis were sealed in screw topped borosilicate glass vials fitted with a PTFE/silicone slit septum. Catalyst cloths were dried in air at 293 K for a minimum of 1 h before reuse in recycling studies with a fresh reactant solution each time.

## 1.2 Product Analysis

### 1.2.1 *Mizoroki-Heck, Suzuki-Miyaura, and Sonogashira Single Use Coupling Reactions*

Gas chromatography (GC) (Young Lin Instrument Co. YL6100 gas chromatograph fitted with a siloxane capillary column (5% phenyl / 95% dimethylpolysiloxane BP-5), length of 30 m, internal diameter of 0.25 mm, coating thickness of 0.25 µm), a starting temperature of 353 K, a hold time of 5 min, a ramp rate 5 K min<sup>-1</sup>, and a final temperature of 573 K, with a hold time of 10 min. Product yield was calculated from GC as the percentage conversion of haloarene to desired coupled product in the recovered reaction solution, all other reagents were used in excess. Product selectivity was calculated as the percentage of desired product molecules produced per molecule of haloarene consumed. Gas chromatography mass spectrometry analysis (GC-MS) (Schimadzu Europa GmbH, GCMS-QP2010 Ultra fitted with an Rxi<sup>®</sup>-5Sil column, length of 30 m, internal diameter of 0.25 mm, coating thickness of 0.25 µm) was conducted with a starting temperature of 353 K, a hold time of 5 min, a ramp rate 5 K min<sup>-1</sup>, and a final temperature of 573 K with a hold time of 10 min. Coupling reaction products were confirmed using authentic samples of biphenyl (99 wt%, Aldrich Chemical Co. Inc.), diphenylacetylene (98 wt%, Aldrich Chemical Co. Inc.), and trans-stilbene (96 wt%, Aldrich Chemical Co. Inc.).

### **1.2.2 Sonogashira and Suzuki-Miyaura Coupling Recycling Experiments**

GC (Bruker Corp. Scion 456 gas chromatograph with a flame ionization detector (FID) fitted with a siloxane capillary column (5% phenyl / 95% dimethylpolysiloxane BP-5), length of 30 m, internal diameter of 0.25 mm, coating thickness of 0.25  $\mu\text{m}$ ) was conducted using high-performance liquid chromatography (HPLC) autosampler vials with a PTFE/silicone slit septum at a starting temperature of 373 K, a hold time of 4 min, a ramp rate of 20 K  $\text{min}^{-1}$ , and a final temperature of 473 K with a hold time of 9 min. Product yield was calculated from GC as the percentage conversion of haloarene to desired coupled product in the recovered reaction solution, all other reagents were used in excess. GC-MS (Shimadzu Europa GmbH, GCMS-QP2010 Ultra fitted with an Rxi<sup>®</sup>-5Sil column, length of 10 m, internal diameter of 0.15 mm, column coating thickness of 0.15  $\mu\text{m}$ ) was conducted at a starting temperature of 303 K and a hold time of 1 min, a ramp rate of 50 K  $\text{min}^{-1}$ , and a final temperature of 573 K, with a hold time of 5 min.

## **2 REFERENCE**

- [1] Scientific Glass Laboratories Ltd. Technical Help, Composition and Corrosion Resistance of Borosilicate Glass 3.3. [http://www.scientificglass.co.uk/pdf/SGL\\_Glass\\_Traps\\_Chemical\\_Composition\\_of\\_Borosilicate\\_glass.pdf](http://www.scientificglass.co.uk/pdf/SGL_Glass_Traps_Chemical_Composition_of_Borosilicate_glass.pdf) (accessed Jan 13, 2016).