A new eco-friendly approach for the preparation of sustainable heterogeneous palladium catalysts from rice husk-derived biogenic silica (RHp-Si and RHu-Si). The designed heterogeneously supported palladium species (RHp-Si-NH2-Pd and RHu-Si-NH2-Pd) were fully characterized and successfully employed as catalysts for various chemical transformations (C–C bond-forming reactions, aerobic oxidations and carbocyclizations). Suzuki-Miyaura transformations were highly efficient in a green solvent system (H2O:EtOH (1:1) with excellent recyclability, providing the cross-coupling products with a wide range of functionalities in high isolated yields (up to 99%). Palladium species (Pd(0)-nanoparticles or Pd(II)) were also efficient catalysts in the green aerobic oxidation of an allylic alcohol and a co-catalytic stereoselective cascade carbocyclization transformation. In the latter case, a quaternary stereocenter was formed with excellent stereoselectivity (up to 27:1 dr).

Rice husk (RH) is a major waste product from the rice industry with high content of silica. This abundant material is a sustainable and cheap raw material and therefore within the context of sustainability. De facto, rice husk ash (RHA) is known to contain 94% silica. Here, silica is a very important component for various industrial and biomedical applications, being high surface area silicates highly desirable and good candidates as catalyst support. For these reasons the development of efficient methods for the preparation of silica and silica based materials are of high interest. In general, the production of silica from RH is energy intensive i.e. obtained by burning RH in a muffle furnace at high temperature (500, 600 or 700 °C). Nevertheless, even though there are some reports on simple and energy-efficient method for the generation of silica from RH, drawbacks such as risk for mineral contamination, several acid and based extraction steps or tedious approaches are encountered. In this context, novel methods for the extraction of silica in an eco-friendly, cost-efficient, scalable and facile approach can be highly attractive. This report discloses the preparation of palladium based multifunctional heterogeneous catalysts from RH-derived silica as support. There are reports on the immobilization of various metals on RH and their use as heterogeneous catalysts for chemical syntheses. In this context, Chang and co-workers...
developed [Pd(NH₃)₄]²⁺-modified nanopore silica, derived from RH and further demonstrated their use in the solvent-free Suzuki-Miyaura cross-coupling reaction. However, some examples of the coupling reactions resulted in very poor reactivity (~4% yield). Within this theme, Gogoi and co-workers also developed a highly efficient RH based Pd(II)-Schiff base complex heterogenous catalyst for the Suzuki-Miyaura coupling reaction in water. Even though the catalyst was recyclable and reusable up to 6 cycles, it successively lost its activity (1st cycle 98% and 6th cycle 90% yield). The same reaction was employed by Boruah et al. by using recyclable Pd(OAc)₂ in neat Water Extract of Rice Straw Ash (WERSA), nevertheless, moderate to high yields (45–90% yields) and low enduring recyclability was observed (1st cycle 88% and 6th cycle 65% yield). Additionally, Liu et al. demonstrated the preparation of porous silica derived from acid leached RH after calcination as support for palladium and cerium (IV) oxide (CeO₂). The catalyst was employed for the catalytic methane combustions. Moreover, Esmaeilpour et al. disclosed the preparation of dendrimer-encapsulated Pd(0) nanoparticles immobilized on nanosilica (nSiO₂-dendrimer-Pd(0)) and their application in the Sonogashira-Hagihara reactions in the absence of any copper and phosphorous ligand in water under aerobic conditions. Despite these notable advances, there is a need to find novel, facile and green approaches to obtain high purity and surface area silica rice husk (RH-Si) for further catalyst design into multifunctional, recyclable and highly efficient heterogenous catalytic systems. Heterogenous catalysts offers several advantages such as allowing the facile and practical recycling of the catalyst, reuse in several cycles without any loss of efficiency and avoiding the leaching of expensive and toxic metals. All of these features characterize a sustainable and eco-friendly technology. Based on the above challenges and our previous experience in developing palladium based heterogenous catalysts for various green chemical transformations, we designed an eco-friendly approach for the preparation of heterogeneous and multifunctional palladium catalysts suitable for a wide spectrum of chemical transformations. The activity and versatility of the designed catalysts was demonstrated in the Suzuki-Miyaura cross-coupling reaction, aerobic oxidation approach of allylic alcohols and stereoselective cascade carbocyclization reactions (Fig. 1a).
Results and Discussion

Initially, RH derived silica was obtained through a previously reported facile and novel approach (Fig. 1b)31. RH was grinded, underwent microwave-assisted extraction and then further purification (washing and calcination) to afford the silica products. Two type of silica materials were prepared, one unrefined biosilicate (RHU-Si, 90% purity, grey color) and the second one, pure biosilicate (RHP-Si, >98% purity, white color). Subsequently, the homogenous palladium catalyst was incorporated onto the RHU-Si and RHP-Si via conjugation with amino groups through a silylation step (RHU-Si-NH2 and RHP-Si-NH2), followed by treatment with the palladium precursor (Li2PdCl4) providing the heterogenous palladium catalysts (RHU-Si-NH2-Pd(II) and RHP-Si-NH2-Pd(II)). These two heterogenous palladium (II) catalysts were simply converted to the corresponding RHU-Si-NH2-Pd(0) and RHP-Si-NH2-Pd(0) by a reduction step (Fig. 1c). The fabricated materials were thoroughly characterized (Fig. 2). Firstly, the porosity and pore size of the RH based materials (RHP-Si, RHU-Si-NH2-Pd(II)/Pd(0) and RHP-Si-NH2-Pd(II)/Pd(0)) were determined by nitrogen physisorption experiments (Figs. 2a and S3−10). Unmodified RHP-Si displayed a Brunauer-Emmet-Teller (BET) with a surface area of ca. 352 m2/g and with mesoporous characteristics (8.0 nm) and pore volume of 0.56 cm3/g (Fig. 2b). However, both surface area and pore volume decreased after palladium incorporation, whilst the pore size distribution changed to macropores (e.g. RHU-Si-NH2-Pd(II) = 163 m2/g−1, 89.4 nm and 0.36 cm3/g−1). Such is a normal behaviour observed in our previous reports, indicating the binding and incorporation of palladium into the material23,27,32. The elemental analysis confirmed the palladium content of the various heterogenous catalysts as 20.30 wt% for RHU-Si-NH2-Pd(II), RHP-Si-NH2-Pd(II) = 19.11 wt%, RHU-Si-NH2-Pd(0) = 19.05 wt% and RHP-Si-NH2-Pd(0) = 16.90 wt%, respectively.

Moreover, the surface area decreased and pore size increased when the Pd(II) was reduced to Pd(0) (e.g. RHP-Si-NH2-Pd(II) = 153 m2/g−1 and 63.6 nm; RHU-Si-NH2-Pd(0) = 144 m2/g−1 and 70.5 nm). X-ray diffraction (XRD) patterns of the RHP-Si displayed a strong broad peak at about 22° 2θ angle indicating its amorphous structure (Fig. 2c). This is also consistent with previous reports on amorphous silica derived from rice husk33. The amorphous characteristics of the RHP-Si could also be confirmed by Scanning electron microscopy (SEM) micrographs (Figure S11). Additionally, Transmission electron microscopy (TEM) of the RHP-Si at different magnifications, at (i) 500 nm and (ii) 200 nm. TEM of the various palladium heterogenous catalysts (e) RHP-Si-NH2-Pd(II) (f) RHU-Si-NH2-Pd(0) (g) RHP-Si-NH2-Pd(II) (h) RHP-Si-NH2-Pd(0).

Upon characterization, the catalytic performance of the designed heterogenous palladium catalysts were further evaluated. The Suzuki cross-coupling reaction was selected as model reaction. The initial reaction between iodo benzene 1a and phenylboronic acid 2a in the presence of potassium carbonate (K2CO3)29 and catalytic amounts of RHU-Si-NH2-Pd(II) (5 mol%) in water (H2O) provided the corresponding diphenyl product 3a in 54% isolated yield after 3 h at 100 °C (Table 1, entry 1). Further screening of the solvents showed that dimethylformamide (DMF) displayed the best efficiency among the investigated (toluene (85%) and ethanol (EtOH) (95%))
cess, we decided to mix H2O and ethanol (EtOH) (1:1) as reaction medium, and to our delight, the reaction proceeded efficiently to afford cinnamic aldehyde in 99% yield (Table 1, entry 5). This improvement could be due to the improved solubility of the substrates with the addition of ethanol than having solely H2O as solvent. It is well-known that silicate is not soluble or show very low solubility in water35. No differences in catalytic activity between the various palladium catalysts were observed (Table 1, entries 5–8), and moreover, a decrease in catalyst amount (from 5.0 to 2.5 mol%) did not negatively impact the reaction efficiency (Table 1, entries 8–11). However, when the amount of the Pd-catalyst was decreased to 0.10 mol% the efficiency was decreased and provided the product 3a with 81% yield (Table 1, entry 12). Enduring the fine-tuning of the reaction, a decrease in reaction temperature and time were further investigated, where 1 h reaction time at 70 °C worked well (Table 1, entries 13–15). However, further decrease of the temperature to 50 °C decreased the efficiency of the reaction (72% yield, Table 1, entry 16).

Table 1. Reaction optimization conditions of the Suzuki cross-coupling reaction. [*] Reaction conditions: Pd-catalyst (mol%), iodobenzene 1a (204.0, 1.0 mmol, 1.0 equiv.), phenylboronic acid 2a (146.3 mg, 1.2 mmol, 1.2 equiv.), K2CO3 (414.6 mg, 3.0 mmol, 3.0 equiv.), solvent (3 mL), 100 °C, 3 h. [b] Yield of purified product (%, b). [c] The reaction was run for 1 h. [d] The reaction was performed at 70 °C. [e] The reaction was run for 1 h at 70 °C. [f] The reaction was run for 1 h at 50 °C.

| Entry | Pd-catalyst (mol%) | Solvent | K2CO3, solvent, 100 °C, 3 h | Yield (%)b |
|-------|-------------------|---------|-----------------|-----------|
| 1     | RHu-Si-NH2-Pd(II) (5) | H2O     | 99              | 54        |
| 2     | RHu-Si-NH2-Pd(II) (5) | toluene | 85              |           |
| 3     | RHu-Si-NH2-Pd(II) (5) | EtOH    | 95              |           |
| 4     | RHu-Si-NH2-Pd(II) (5) | DMF     | 98              |           |
| 5     | RHu-Si-NH2-Pd(II) (5) | H2O:EtOH (1:1) | 99          |           |
| 6     | RHu-Si-NH2-Pd(II) (5) | H2O:EtOH (1:1) | 98          |           |
| 7     | RHu-Si-NH2-Pd(0) (5)  | H2O:EtOH (1:1) | 98          |           |
| 8     | RHu-Si-NH2-Pd(0) (5)  | H2O:EtOH (1:1) | 99          |           |
| 9     | RHu-Si-NH2-Pd(0) (1)  | H2O:EtOH (1:1) | 98          |           |
| 10    | RHu-Si-NH2-Pd(0) (0.5) | H2O:EtOH (1:1) | 98          |           |
| 11    | RHu-Si-NH2-Pd(0) (0.25) | H2O:EtOH (1:1) | 99          |           |
| 12    | RHu-Si-NH2-Pd(0) (0.10) | H2O:EtOH (1:1) | 98          |           |
| 13    | RHu-Si-NH2-Pd(0) (0.25) | H2O:EtOH (1:1) | 98          |           |
| 14    | RHu-Si-NH2-Pd(0) (0.25) | H2O:EtOH (1:1) | 98          |           |
| 15    | RHu-Si-NH2-Pd(0) (0.25) | H2O:EtOH (1:1) | 98          |           |
| 16    | RHu-Si-NH2-Pd(0) (0.25) | H2O:EtOH (1:1) | 72          |           |

to afford 3a in 98% yield (Table 1, entries 2–4). However, enduring our vision in designing an eco-friendly process, we decided to mix H2O and ethanol (EtOH) (1:1) as reaction medium, and to our delight, the reaction provided the product 3a in 99% yield (Table 1, entry 5). This improvement could be due to the improved solubility of the substrates with the addition of ethanol than having solely H2O as solvent. It is well-known that silicate is not soluble or show very low solubility in water35. No differences in catalytic activity between the various palladium catalysts were observed (Table 1, entries 5–8), and moreover, a decrease in catalyst amount (from 5.0 to 0.25 mol%) did not negatively impact the reaction efficiency (Table 1, entries 8–11). However, when the amount of the Pd-catalyst was decreased to 0.10 mol% the efficiency was decreased and provided the product 3a with 81% yield (Table 1, entry 12). Enduring the fine-tuning of the reaction, a decrease in reaction temperature and time were further investigated, where 1 h reaction time at 70 °C worked well (Table 1, entries 13–15). However, further decrease of the temperature to 50 °C decreased the efficiency of the reaction (72% yield, Table 1, entry 16). Delighted by these findings, the substrate scope of the reaction was further explored, which showed that the reaction tolerated a wide range of functionalities with both aryl iodide 1a and aryl bromide 1b and various boronic acids 2 (Table 2). Nevertheless, a slight decrease in yields was observed for the reaction between bromobenzene 1b and phenylboronic acid 2a and between the iodobenzene 1a and 4-(trifluoromethyl) phenylboronic acid 2e providing products 3a and 3f (85 and 88% yields, Table 2, entries 2 and 8). Overall, the coupling reaction showed high efficiency and provided the coupling products in high yields (up to 99%). Since the recyclability of a heterogenous catalyst is an eminence feature both in the economic and environmental aspects, the recyclability and reusability of the devised palladium heterogenous catalysts were further studied. The heterogenous systems could be recycled for 6 consecutive cycles without losing any efficiency (Fig. 3a). Notable all the four heterogenous palladium catalysts (RHu-Si-NH2-Pd(II), RHp-Si-NH2-Pd(II) only, RHu-Si-NH2-Pd(0), RHp-Si-NH2-Pd(0)) were recycled at least one cycle. However RHu-Si-NH2-Pd(0) catalyst was selected for further recycling study. Moreover, no leaching was observed as determined by elemental analysis performed on the filtrate after the hot filtration and after the completion of the reaction.

To further broaden the application of the synthesized Pd catalyst, the selected optimum system (RHu-Si-NH2-Pd(0)) was employed in the aerobic oxidation of cinnamyl alcohol 4 to the corresponding aldehyde as model reaction43. The reaction proceeded efficiently to afford cinnamic aldehyde 5 (>99%) as only product after 48 h, in toluene at 70 °C, employing 5 mol% of the catalyst in the presence of oxygen gas (Fig. 3b). In addition to the cross-coupling and oxidation reactions, the reaction portfolio was further expanded for the application of the heterogenous palladium catalyst in amine/palladium co-catalyzed carbocyclization reactions (Fig. 3c). The reaction was conducted between cinnamic aldehyde 5 and propargylcyanomalonate 6 in the presence of catalytic amount of palladium heterogenous catalyst (RHu-Si-NH2-Pd(II) and RHu-Si-NH2-Pd(II) (5 mol%)) and the chiral amine catalyst 7 (20 mol%). The chemical transformation proceeds via formation of the enamine intermediate35, and subsequent stereoselectivity nucleophilic enamine addition provided the carbocycle 8, in high yields (up to 82%) and diastereoselectivities (up to 27:1 dr determined through 1H-NMR analysis and the e.r. where not determined. However, the obtained optical rotation ([α]D = −6.31 (c = 1.0 CHCl3)) resembles to the previously reported ee of >97.5:2.5 er) (Fig. 3c)33. These all examples highlight the versatility and simplicity of the devised RH-based heterogenous palladium catalyst employed in various relevant chemical transformations.
A highly efficient Pd-heterogeneous catalyst from the biomass-based Rice husk waste was synthesized. The novel preparation approach integrating the valorization of renewable starting materials represents a green, facile and simple eco-friendly method for catalyst design. The devised heterogeneous palladium catalysts were proved to be highly versatile, being successfully employed in Suzuki-Miyaura cross-couplings (high product yields, up to 99%, wide range of functionalities), the aerobic oxidation of cinnamoyl alcohol and the amine catalyzed stereoselective

| Entry* | Ar1-X | Ar2-B(OH)2 | Product 3 | Yield (%)b |
|--------|--------|------------|-----------|------------|
| 1      | 1a     | 2a         | 3a        | 98         |
| 2      | 1b     | 2a         | 3a        | 85         |
| 3      | 1a     | 2b         | 3b        | 95         |
| 4      | 1a     | 2c         | 3c        | 99         |
| 5      | 1b     | 2c         | 3c        | 92         |
| 6      | 1c     | 2d         | 3d        | 98         |
| 7      | 1a     | 2d         | 3e        | 94         |
| 8      | 1a     | 2e         | 3f        | 88         |
| 9      | 1d     | 2a         | 3g        | 99         |
| 10     | 1c     | 2b         | 3h        | 99         |

Table 2. Scope of the Suzuki coupling reaction catalyzed by RHP-Si-NH2-Pd(0). [a] Reaction conditions: RHP-Si-NH2-Pd(0) (1.6 mg, 0.25 mol%), aryl iodine 1 (1.0 mmol, 1.0 equiv.), arylboronic acid 2 (1.2 mmol, 1.2 equiv.), K2CO3 (414.6 mg, 3.0 mmol, 3.0 equiv.), H2O:EtOH (1:1, 3 mL), 70 °C, 1 h. [b] Yield of purified product 3 after silica chromatography.

Conclusion
A highly efficient Pd-heterogeneous catalyst from the biomass-based Rice husk waste was synthesized. The novel preparation approach integrating the valorization of renewable starting materials represents a green, facile and simple eco-friendly method for catalyst design. The devised heterogeneous palladium catalysts were proved to be highly versatile, being successfully employed in Suzuki-Miyaura cross-couplings (high product yields, up to 99%, wide range of functionalities), the aerobic oxidation of cinnamoyl alcohol and the amine catalyzed stereoselective
carbocyclization reaction (cyclopentene derivatives obtained in high yields and stereoselectivities, up to 82%, 27:2 dr). Additionally, the Pd system was highly recyclable and could be reused after simple centrifugation in 6 cycles without any loss of efficiency. The disclosed protocol represents a green and sustainable chemical approach that may find relevant and suitable future applications in additional chemical transformations.

Methods

General and materials. Chemicals and solvents were either purchased puriss p. a. from commercial suppliers or were purified by standard techniques. Commercial reagents were used as purchased without any further purification. Aluminum sheet silica gel plates (Fluka 60 F254) were used for thin-layer chromatography (TLC), and the compounds were visualized by irradiation with UV light (254 nm) or by treatment with a solution of phosphomolybdic acid (25 g), Ce(SO4)2·H2O (10 g), conc. H2SO4 (60 mL), and H2O (940 mL), followed by heating. 1H NMR spectra were recorded on a Bruker Avance (500 MHz or 400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance resulting from incomplete deuterium incorporation as the internal standard (CDCl3: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, br = broad, m = multiplet), and coupling constants (Hz), integration. 13C NMR spectra were recorded on a Bruker Avance (125.8 MHz or 100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl3: δ 77.16 ppm). Gas sorption measurements were carried out on a Micrometrics ASAP2020 analyzer and recorded at 77 K. N2 adsorption measurements on the RH-Si were performed at 77 K by using a Micromeritics ASAP 2000 volumetric adsorption analyzer. The samples were degassed for 24 h at 130 °C under vacuum (Po < 10−2 Pa) and subsequently analyzed. Surface area of the RH-Si was calculated according to the Brunauer-Emmet-Teller (BET) equation. Mean pore size diameter and pore volumes were obtained from porosimetry data by using Barret-Joyner-Halenda (BJH) method. Wide-angle X-ray diffraction experiments were recorded on a Pan-Analytic/Philips X’pert MRD diffractometer (40 kV , 30 mA) with CuKα (λ = 0.15418 nm) radiation. Scans were performed over a 2θ = 10–80 °C at step size of 0.0188 with a counting time per step of 5 s. TEM image of the RH-Si was obtained on JEM 2010F (JEOL) and Phillips Analytical FEI Tecnai 30 microscopes. All other TEM experiments were carried out on a 200 kV JEOL JEM-2100F field-emission electron microscope equipped with an ultra-high-resolution pole piece. A Gatan ultra-high tilt tomography holder was used. TEM samples were prepared by crushing, and the tomography data was acquired between −60° and +60° with 1° increments. Each image per tilt angle was recorded with a Gatan Ultrascan 1000 camera. The data acquisition was assisted by a commercial tomography packed, TEMography (version 2.15.07) developed by JEOL System Technology Co. Ltd. SEM micrographs of the RH-Si was obtained on JEM 1010F (JEOL) and Phillips Analytical FEI Tecnai 30 microscopes. Elemental analyses were carried out by Medac LTD Analytical and chemical consultancy services (United Kingdom) by ICP-OES.

Preparation of the RH₄-Si-Pd-heterogeneous catalysts Rice husk silica preparation (RH₄-Si). The particle size of the rice husk (RH) was reduced by grinding in a Retsch-PM-100 planetary ball mill using a 125 mL reaction chamber end eighteen stainless steel balls (10 mm diameter, 5 g weight). Milling was conducted at 350 rpm for 10 min. The obtained silica from RH was treated to microwave assisted extraction in ETHOS-ONE. The RH was then refluxed in a 0.29 M HCl solution at 300 W for 30 min. The silica solution was...
cooled to room temperature, filtered and washed with distilled water and then dried in oven at 100 °C for 24 h. The resulting solid was calcined in a furnace at 550 °C for 4 h to obtain pure silica (RH₅-Si).

**General preparation of the RH₅-Si-NH₂.** The preparation of the RH₅-Si-NH₂-Pd-catalyst started with the amino functionalization of the RH₅-Si. Dry toluene (20 mL) was added to the RH₅-Si (1.38 g, 22.2 mmol mg, 1.0 equiv.), followed by addition of a solution of 3-aminopropytrimethoxy silane (7.8 mL, 44.4 mmol, 2.0 equiv.) in toluene (10 mL). The mixture was stirred under nitrogen for 10 minutes, and then refluxed for 24 h. The mixture was allowed to cool to room temperature and the solid was collected by filtration and washed several times with toluene, ethanol, aceton and dichloromethane to remove any unreacted precursor. The material was further dried under vacuum giving RH₅-Si-NH₂ (1.405 g).

**General preparation of the RH₅-Si-NH₂-Pd(II).** The amino-functionalized RH₅-Si-NH₂ (1.0 g) was suspended in deionized water (15 mL) and the solution was pH-adjusted to pH 9, by the use of 0.1 N LiOH. In parallel Li₂PdCl₄ (600 mg) was diluted in deionized water (10 mL) and the solution was pH-adjusted to pH 9, by the use of 0.1 N LiOH. This solution was transferred to the flask containing RH₅-Si-NH₂ solution. The reaction was stirred at room temperature for 24 h. Subsequently, the suspension was then centrifuged, and the solid material was further washed with water (3 × 40 mL) and acetone (3 × 40 mL) and centrifuged. The material was then dried overnight under vacuum providing RH₅-Si-NH₂-Pd(II) (1.408 g). Elemental analysis on the Pd content were 20.30 wt.% for RH₅-Si-NH₂-Pd(II) and 19.11 wt.% for RH₅-Si-NH₂-Pd(II).

**General preparation of the RH₅-Si-NH₂-Pd(0).** RH₅-Si-NH₂-Pd(II) (500 mg) was suspended in deionized water (15 mL), followed by slow addition of a solution of NaBH₄ (310.2 mg, 8.2 mmol) in water (5 mL) at room temperature. The reaction was stirred at room temperature for 30 minutes. Afterwards the solution was centrifuged and the solid diluted with water (3 × 40 mL) and centrifuged. The material was then dried overnight under vacuum providing RH₅-Si-NH₂-Pd(0). Elemental analysis on Pd content were 19.05 wt.% for the RH₅-Si-NH₂-Pd(0) and 16.90 wt.% for RH₅-Si-NH₂-Pd(0), respectively.

**General procedure for Pd-catalyst catalyzed Suzuki-Miyaura reaction (Table 1).** A microwave vial equipped with a magnetic stir bar was charged with the Pd-catalyst (mol%), phenylboronic acid 2a (146.4 mg, 1.2 mmol, 1.2 equiv.), K₂CO₃ (414.6 mg, 3.0 mmol, 3.0 equiv.), followed by addition of solvent (3.0 mL). Subsequently, iodobenzene 1a (204.0 mg, 1.0 mmol, 1.0 equiv.) was added and the reaction mixture heated and run for the temperature and time stated at Table 1. Next, the reaction mixture was either centrifuged and the solid diluted with acetone (3 × 10 mL) and centrifuged and then concentrated before purification or directly subjected to flash chromatography on silica (petroleum ether/EtOAc 100–90%) affording the pure product 3a.

**Procedure for RH₅-Si-NH₂-Pd (0) catalyst catalyzed Suzuki-Miyaura reaction (Table 2).** A microwave vial equipped with a magnetic stir bar was charged with RH₅-Si-NH₂-Pd(0) catalyst (1.6 mg, 0.0025 mmol, 0.25 mol%), phenylboronic acid 2a (1.2 mmol, 1.2 equiv.), K₂CO₃ (414.6 mg, 3.0 mmol, 3.0 equiv.), followed by addition of H₂O:EtOH (1:1, 3.0 mL). Subsequently, aryl halide 1 (1.0 mmol, 1.0 equiv.) was added and the reaction mixture heated to 70 °C and stirred for 1 h. Next, the reaction mixture was either centrifuged and the solid diluted with acetone (3 × 10 mL) and centrifuged and then concentrated before purification or directly subjected to flash chromatography on silica (petroleum ether/EtOAc, 100–90%) affording the pure products 3.

**Procedure for the recycling of RH₅-Si-NH₂-Pd(0) catalyst.** A microwave vial equipped with a magnetic stir bar was charged with RH₅-Si-NH₂-Pd(0) catalyst (6.3 mg, 0.01 mmol, 1.0 mol%), phenylboronic acid 2a (1.2 mmol, 1.2 equiv.), K₂CO₃ (414.6 mg, 3.0 mmol, 3.0 equiv.), followed by addition of H₂O:EtOH (1:1, 3.0 mL). Subsequently, iodobenzene 1a (204.0 mg, 1.0 mmol, 1.0 equiv.) was added and the reaction mixture heated to 70 °C and stirred for 1 h. Next, the reaction mixture was centrifuged and the solid diluted with acetone (3 × 10 mL) and centrifuged. The collected liquid was concentrated and purified by flash chromatography on silica (petroleum ether/EtOAc 100–90%) affording the pure product 3a. The solid catalyst was diluted with water (10 mL) in order to remove remaining base and centrifuged. The solid catalyst was further diluted with acetone (2 × 10 mL) and centrifuged. Afterwards the solid heterogeneous catalyst was dried under vacuum and then further used in next cycle. Notable all the four heterogenuous palladium catalysts (RH₅-Si-NH₂-Pd(II), RH₅-Si-NH₂-Pd(P0), RH₅-Si-NH₂-Pd(II), RH₅-Si-NH₂-Pd(II)) were recycled at least one cycle. RH₅-Si-NH₂-P(0) was selected for further cycle studies.

**Typical procedure for the hot-filtration test.** A microwave vial equipped with a magnetic stir bar was charged with pure RH₅-Si-NH₂-Pd(0) catalyst (1.6 mg, 0.025 mmol%), phenylboronic acid 2a (146.4 mg, 1.2 mmol, 1.2 equiv.), K₂CO₃ (414.6 mg, 3.0 mmol, 3.0 equiv.), followed by addition of solvent (3.0 mL). Subsequently, iodobenzene 1a (204.0 mg, 1.0 mmol, 1.0 equiv.) was added and the reaction mixture heated to 70 °C. RH₅-Si-NH₂-Pd(0) catalyst was removed through centrifugation after 30% conversion was reached and the solid free filtrate was allowed to stir for 24 h reaction conditions. Analysis of the reaction mixture showed that no further conversion of the substrate had occurred.

**Procedure for the catalytic aerobic oxidation.** To a suspension of RH₅-Si-NH₂-Pd(0) (5 mol% Pd to 4, 7.6 mg) in toluene (0.5 mL) placed in an oven-dried microwave vial equipped with a magnetic stir bar was charged with cinnamyl alcohol 4 (32.3 mg, 0.24 mmol, 1.2 equiv.). The vial was capped, evacuated and an O₂-balloon was
connected to the reaction vessel. The reaction mixture was stirred at 70 °C for 48 h affording the corresponding cinamic aldehyde 5.

**General procedure for the combined transition metal/amine catalytic reaction using propargylcyanomalonate.** An oven-dried microwave vial equipped with a magnetic stir bar was charged with propargylcyanomalonate 6 (16.1 mg, 0.12 mmol, 1.2 equiv.) and Pd-catalyst (5 mol%, 0.005 mmol), followed by addition of toluene (0.100 mL) and the resulting mixture was stirred at room temperature for 5 min. In parallel to the above procedure, an oven-dried vial was charged with the cinamic aldehyde 5 (13 mg, 0.1 mmol, 1.0 equiv.), aminocatalyst 7 (6.5 mg, 0.02 mmol, 20 mol%) and followed by addition of toluene (0.15 mL), after stirring at room temperature for additional 5 min, the resulting mixture was transferred to the vial containing the mixture of palladodium catalyst and propargylcyanomalonate via a syringe. (Total volume of Toluene = 0.25 mL, Final concentration = 0.8 M to aldehyde). The reaction was stirred for 24 h at room temperature. The conversions and diastereomeric ratio were monitored by 1H NMR analysis of the crude mixture. Upon completion, the mixture was subjected to flash chromatography on silica (pentane/EtOAc) affording the pure products in 8.

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A.C., R.L., S.A. and A.M.B. designed the research; S.A, A.F. and A.M.B. performed the research and C.-W. Tai performed the TEM experiments and analysis. A.C., R.L., S.A. and A.M.B. wrote the paper. All the authors analyzed the data.

**Competing interests**
The authors declare no competing interests.

**Additional information**
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