Supplementary Materials: Immobilized Palladium Nanoparticles on Zirconium Carboxy-Aminophosphonates Nanosheets as an Efficient Recoverable Heterogeneous Catalyst for Suzuki- Miyaura and Heck Coupling

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Figure S1. IR spectra of ZPGly and Pd@ZPGly-1.

The IR spectrum of ZPGly shows the bands ascribable to the stretching and bending of the O-H bond at 3424 cm⁻¹ and 1640 cm⁻¹, due to the hydration water molecules. The bands at 3002 and 2995 cm⁻¹ are due to the C-H stretching. The broad band centered at 2600 cm⁻¹ is characteristic of a R₃-NH⁺ group, proving the presence of protonated amino groups. The band at 1739 cm⁻¹ is associated with the C=O stretching of the -COOH group, accompanied by the bands at 1427 (O-H bending) and 1244 cm⁻¹ (C-O stretching). The bands from 950–1200 cm⁻¹ are related to the P-O stretchings, whereas in the region below 900 cm⁻¹, a number of bands are found, which are not straightforwardly assigned (various bending modes, Zr-O stretchings).

In the sample Pd@ZPGly-15, typical bands of the COOH group disappear, while the typical bands of the COO⁻ group appear at 1567 cm⁻¹ and at 1370 cm⁻¹, ascribable to asymmetric and symmetric stretching of COO⁻. These findings suggest that the proton was transferred to the propylamine and that both palladium ions and propylammonium ions take part in neutralizing the negative charge of carboxylate groups.
Figure S2. TEM images of Pd@ZPGly-1 (a), Pd@ZPGly-1R (b), Pd@ZPGly-7 (c), Pd@ZPGly-7R (d) and Pd@ZPGly-15 at a low magnification.
Figure S3. STEM (above) and HRTEM (below) images of Pd@ZPGly-15. The size distribution of the smaller population of Pd nanoparticles on Pd@ZPGly-15 is also reported.

**Procedure for hot filtration test in the Suzuki reaction in aq. EtOH azeotrope with Pd@ZPGly-15 catalyst:**

In a vial, Pd@ZPGly-15 catalyst (0.47 mg, 2.11 mmol of Pd per g, 0.1 mol%), phenylboronic acid (2a, 134 mg, 1.1 mmol), K$_2$CO$_3$ (167 mg, 1.10 mmol), 4-bromotoluene (1a, 171 mg, 1 mmol) and ethanol 96% (2.4 mL) were placed. The reaction mixture was stirred at 80 °C for 20 min (conv. 71%), and the hot filtration was performed. K$_2$CO$_3$ (167 mg) was added again and the reaction mixture stirred at 80 °C.

- Reaction time 1 h; Conv. 74%
- Reaction time 24 h; Conv. 74%

**Procedure for the homogeneous Suzuki reaction in aq. EtOH azeotrope performed with Pd(OAc):**

The amount of Pd(OAc)$_2$ is comparable to that which leached during the reaction with Pd@ZPGly (11 ppm, Table 3, Entry 3)

In a vial, phenylboronic acid (2a, 134 mg, 1.1 mmol), K$_2$CO$_3$ (167 mg, 1.10 mmol), 4-bromotoluene (1a, 171 mg, 1 mmol), ethanol 96% (2.4 mL) and Pd(OAc)$_2$ (1.7·10$^{-5}$ mmol, 3.9 μL of a solution of 1 mg/1 mL in acetone) were placed. The reaction mixture was stirred at 80 °C for 24 h.

- Reaction time 1 h; Conv. 33%
- Reaction time 24 h; Conv. 41%