Experimental procedures for the synthesis the PdNPs stabilized by the dendrimers, complexation of Pd(OAc)$_2$, by cyclic voltammetry, and transmission electron microscopy (TEM)

Cyclic voltammetry measurements: All electrochemical measurements were recorded under nitrogen atmosphere. Conditions: solvent: chloroform/methanol (2:1); temperature: 20ºC; supporting electrolyte: [nBu$_4$N][PF$_6$] 0.1M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: FeCp$_2^*$ (Cp$^*$= $\eta^5$-C$_5$Me$_5$); scan rate: 0.200 Vs$^{-1}$.

Gas Chromatography: GC data were recorded on a Hewlett Packard 5890 Series II gas chromatograph, equipped with a Stabilwax® (Crossband® Carbowax®-PEG) column and a flame ionization detector. For all substrates Helium was used as the carrier gas. The injector and detector temperature were 240 ºC.

Transmission Electron Microscopy (TEM): Samples were prepared placing a drop of a 4.41x10$^{-4}$ M solution (CHCl$_3$/MeOH 2:1) of palladium nanoparticles (concentration in mol Pd) on a holey-carbon-coated Cu TEM grid.

General procedure for the preparation of PdNPs (these procedures are described using preparation of DSN-G$_0$ as an example): 2 mL of a 3x10$^{-4}$M solution of dendrimer G$_0$ (2.0 mg, 5.87x10$^{-4}$ mmol) in chloroform was placed in a Schlenk flask under nitrogen. 1.2 mL of a 4.5x10$^{-3}$M chloroform solution of Pd(OAc)$_2$ (1.2 mg, 5.28x10$^{-3}$ mmol, 1 equiv. per triazole) was added. Chloroform (0.8 mL) and methanol (2 mL) were added in order to obtain a solution 8.82x10$^{-4}$ M (in Pd), 2:1 (CHCl$_3$/MeOH).
The solution was stirred for 16 h and the yellow solution turned to golden brown indicating the nanoparticle formation.

**General procedure for the extraction of the PdNPs by alkanethiols:** The alkanethiol ligand (2 equiv. per Pd) was added to the DSN or DEN solution and the reaction mixture was stirred under nitrogen, at room temperature for 1h. After removing the solvent under vacuum the crude product was washed several times with acetone, in order to remove the dendrimers and free alkanethiol. The PdNP-thiolate were obtained as black powder.

**Suzuki reactions with DSN or DENs:** In a Schlenck flask, the nanoparticles were freshly prepared in order to obtain a solution 8.82x10⁻⁴ M (in Pd), in CHCl₃/MeOH (2:1) and NaOAc, phenylboronic acid and iodobenzene were successively added. The solution was allowed to stir under N₂ at 25°C.

**Suzuki reactions with Thiol-PdNPs:** In a Schlenck flask, the nanoparticles were dissolved in THF/H₂O (2:1) and NaOH, phenylboronic acid and iodobenzene were successively added. The solution was allowed to stir under N₂ at 25°C.

**Calculation of the Turn Over Frequency (TOF):** several samples of the reaction solution were extracted at different times of reaction, and analyzed by GC.

**Calculation of the Turn Over Number (TON):** determined based on the yield of diphenyl.
Cyclic Voltammetry Data

Titrations of Pd(OAc)$_2$ followed by cyclic voltammetry (CV): General method: The supporting electrolyte was introduced into the electrochemical cell containing the working electrode, the reference electrode and the counter electrode. After dissolving in chloroform/methanol (2:1), a blank voltammogram was recorded to check the working electrode. A chloroform/methanol (2:1) solution of dendrimer and internal reference were added to the cell, and the CV was recorded. Then, small amounts of a chloroform solution of Pd(OAc)$_2$ was added with a microsyringe. After each addition, the solution was degassed, and the CV was recorded. The appearance and progressive increase of a new wave was observed, while the initial wave decreased and finally disappeared. When the initial wave had completely disappeared, addition of the Pd(OAc)$_2$ solution was continued until reaching twice the volume already introduced. Conditions: solvent: chloroform/methanol (2:1); temperature: 20ºC; Supporting electrolyte: $[n$Bu$_4$N][PF$_6$] 0.1M; working and counter electrodes: Pt; quasi-reference electrode: Ag; internal reference: FeCp$_2^*$; scan rate: 0.200 Vs$^{-1}$. 
Titration of Pd(OAc)$_2$ with poly-1,2,3-triazolylferrocenyl dendrimer G$_0$

**Figure S.I.1.** a) CV of G$_0$ (c = 1.47x10$^{-4}$ M) before addition Pd(OAc)$_2$; b) CV of G$_0$ during titration of Pd(OAc)$_2$ (0.5 equiv. per triazole); c) CV of G$_0$ at the end of titration of Pd(OAc)$_2$ (1 equiv. per triazole).

**Figure S.I.2.** Titration of Pd(OAc)$_2$ with G$_0$ (c = 1.47x10$^{-4}$ M). Decrease of the intensity of the initial CV wave (■) and increase of the new CV wave (▲) vs the number of equiv. of Pd(OAc)$_2$ added per Dendrimer G$_0$. 
Titration of Pd(OAc)$_2$ with poly-1,2,3-triazolylferrocenyl dendrimer G$_1$

**Figure S.I.3.** a) CV of G$_1$ (c = 4.89x$10^{-4}$ M) before addition Pd(OAc)$_2$; b) CV of G$_1$ during titration of Pd(OAc)$_2$ (0.6 equiv. per triazole); c) CV of G$_1$ at the end of titration of Pd(OAc)$_2$ (1 equiv. per triazole).

**Figure S.I.4.** Titration of Pd(OAc)$_2$ with G$_1$ (c = 4.89x$10^{-4}$ M). Decrease of the intensity of the initial CV wave (■) and increase of the new CV wave (▲) vs the number of equiv. of Pd(OAc)$_2$ added per Dendrimer G$_1$. 
Titration of Pd(OAc)$_2$ with poly-1,2,3-triazolylferrocenyl dendrimer G$_2$

*Figure S.I.5.* a) CV of G$_2$ (c = $1.63 \times 10^{-5}$ M) before addition Pd(OAc)$_2$; b) CV of G$_2$ during titration of Pd(OAc)$_2$ (0.65 equiv. per triazole); c) CV of G$_2$ at the end of titration of Pd(OAc)$_2$ (1 equiv. per triazole).

*Figure S.I.6.* Titration of Pd(OAc)$_2$ with G$_2$ (c = $1.63 \times 10^{-5}$ M). Decrease of the intensity of the initial CV wave (■) and increase of the new CV wave (▲) vs the number of equiv. of Pd(OAc)$_2$ added per Dendrimer G$_2$. 
Transmission Electron Microscopy (TEM) data

**Figure S.I.7.** DEN-G₀: a) TEM image and b) size distribution.

**Figure S.I.8.** DEN-G₁: a) TEM image and b) size distribution.

**Figure S.I.9.** DEN-G₂: a) TEM image and b) size distribution.
**Figure S.I.10.** a) TEM image of PdNPs extracted from DSN-G₀ with undodecanethiol and b) size distribution.

**Figure S.I.11.** a) TEM image of PdNPs extracted from DEN-G₁ with hexanethiol and b) size distribution.

**Figure S.I.12.** a) TEM image of PdNPs extracted from DEN-G₂ with hexanethiol and b) size distribution.