Catalytically Efficient Palladium Nanoparticles Stabilized by "Click" Ferrocenyl Dendrimers

Cátia Ornelas, Lionel Salmon, Jaime Ruiz Aranzaes, Didier Astruc

Supplementary Information

Cyclic Voltammetry (CV), UV-Vis spectroscopy, ^{1}H NMR and Transmition Electron Microscopy (TEM) data.

Cyclic voltammetry measurements: All electrochemical measurements were recorded under nitrogen atmosphere. Conditions: solvent: Chloroform/Methanol (2:1); temperature: 20ºC; Supporting electrolyte: $[n\mathrm{Bu_4N}][\mathrm{PF_6}]$ 0.1M; working and counter electrodes: Pt; reference electrode: Ag; internal reference: $\mathrm{FeCp_2}^*$ ($\mathrm{Cp}^* = \eta^5\text{-}\mathrm{C_5Me_5}$); scan rate: 0.200 $\mathrm{Vs^{-1}}$.

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 4.41×10^{-4} M solution ($\mathrm{CHCl_3}$/MeOH 2:1) of palladium nanoparticles (concentration in mol Pd) on a holey-carbon-coated Cu TEM grid. The size of the nanoparticles was measured using the software ***sigmascanpro*** (for each sample, about 100 nanoparticles were measured). (The theoretical diameter of the palladium nanoparticles were calculated using the equation $n = 4\pi r^3 / 3V_g$, where n is the number of Pd atoms, r is the radius of the Pd nanoparticle and V_g is the volume of one Pd atom (15 Å^3))[12]

General procedure for the preparation of PdNPs (the procedure is described using preparation of DSN-G$_0$ as an example):

<u>Method 1</u>: 2 mL of a 3×10^{-4}M solution of dendrimer G_0 (2.0 mg, 5.87×10^{-4} mmol) in chloroform was placed in a schlenk flask under nitrogen. 1.2 mL of a 4.5×10^{-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 5 minutes and $NaBH_4$ (2 mg, $5.87x10^{-2}$ mmol, 10 equiv. *per* Pd) was added and the yellow solution turned to golden brown indicating the nanoparticle formation.

Method 2: 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.

Hydrogenation reactions: In a schlenck flask, the nanoparticles were freshly prepared in order to obtain a solution $8.82x10^{-4}$ M (in Pd), in $CHCl_3$/MeOH (2:1) and 1000 equiv. of the substrate was added. The schlenck was filled with H_2 (1 atm) and the solution was allowed to stir at 25ºC. **Re-using the catalyst:** substrate was added to the reaction solution until the catalyst was no longer active.

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

Calculation of the Turn Over Number (TON): The sum of substrate that reacted in all the catalytic cycles effectuated, after analyzing the final reaction solution.

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: $[n\mathrm{Bu}_4\mathrm{N}][\mathrm{PF}_6]$ 0.1M; working and counter electrodes: Pt; quasi-reference electrode: Ag; internal reference: $FeCp_2$*; scan rate: 0.200 Vs^{-1}.

Table 1. Cyclic voltammetry results of the recognition of the $Pd(OAc)_2$ by the poly-1,2,3-triazolylferrocenyl dendrimers.

			Recognition of $Pd(OAc)_2$		
Dendrimer	Number of triazole units (interior + exterior)	$E_{1/2}$[a] (E_{pa}-E_{pc}) (V)	$E_{1/2}$ (E_{pa}-E_{pc}) (V)	$\Delta E_{1/2}$[b] (V)	$K_{(0)}/K_{(+)}$[c]
1- G_0	9	0.540 (0.050)	0.640 (0.030)	-0.100	53
2- G_1	36	0.540 (0.030)	0.625 (0.020)	-0.085	29
3- G_2	117	0.540 (0.030)	0.595 (0.020)	-0.055	9

[a] $E_{1/2} = (E_{pa}+E_{pc})/2$ *vs.* $FeCp_2$* (in V). Electrolyte: $[n\mathrm{Bu}_4\mathrm{N}][\mathrm{PF}_6]$ 0.1M; solvent: chloroform/methanol (2:1); working and counter electrodes: Pt; quasi-reference electrode: Ag; internal reference: $FeCp_2$*; scan rate: 0.200 Vs^{-1}; 20°C. [b] Difference between values of $E_{1/2}$ before (3rd column) and after (4th column) titration. [c] Ratios of apparent association constants; error $\leq$ 10%; $\Delta E_{1/2} = 0.058 \log(K_{(0)}/K_{(+)})$at 20°C.[E.S.I.1]

[E.S.I.1] Miller, S. R.; Gustowski, D. A.; Chen, Z.-H.; Gokel, G. W.; Echegoyen, L.; Kaifer, A. E. *Anal. Chem.* **1988**, *60*, 2021-2024.

Titration of $Pd(OAc)_2$ with poly-1,2,3-triazolylferrocenyl dendrimer G_0

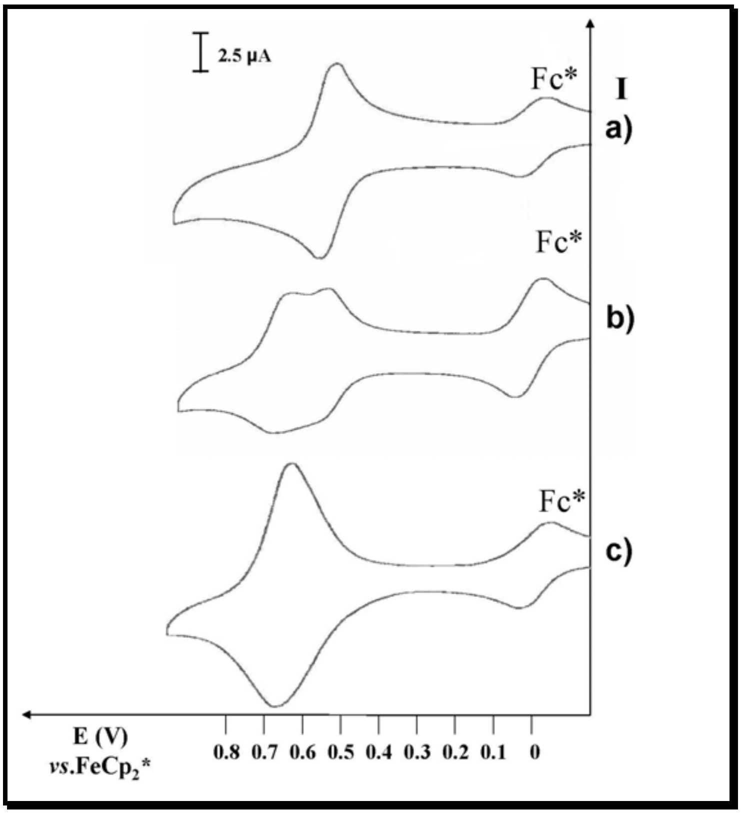


Figure 1. a) CV of $\mathbf{G_0}$ (c = 1.47×10^{-4} M) before addition $Pd(OAc)_2$; b) CV of $\mathbf{G_0}$ during titration of $Pd(OAc)_2$ (0.5 equiv. *per* triazole); c) CV of $\mathbf{G_0}$ at the end of titration of $Pd(OAc)_2$ (1 equiv. *per* triazole).

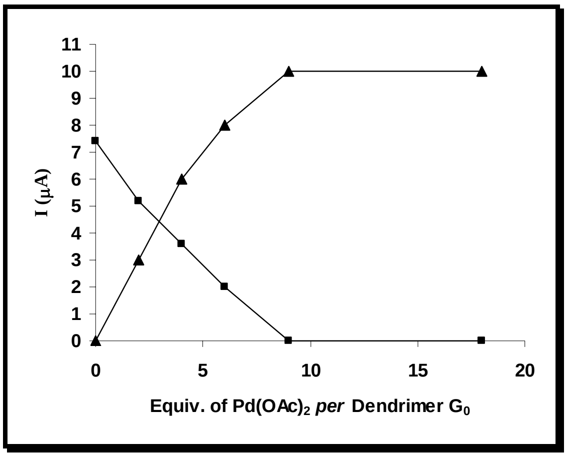


Figure 2. Titration of $Pd(OAc)_2$ with $\mathbf{G_0}$ (c = 1.47×10^{-4} M). Decrease of the intensity of the initial CV wave (■) and increase of the new CV wave (▲) vs the number of equiv. of $Pd(OAc)_2$ added per Dendrimer $\mathbf{G_0}$.

Titration of $Pd(OAc)_2$ with poly-1,2,3-triazolylferrocenyl dendrimer G_1

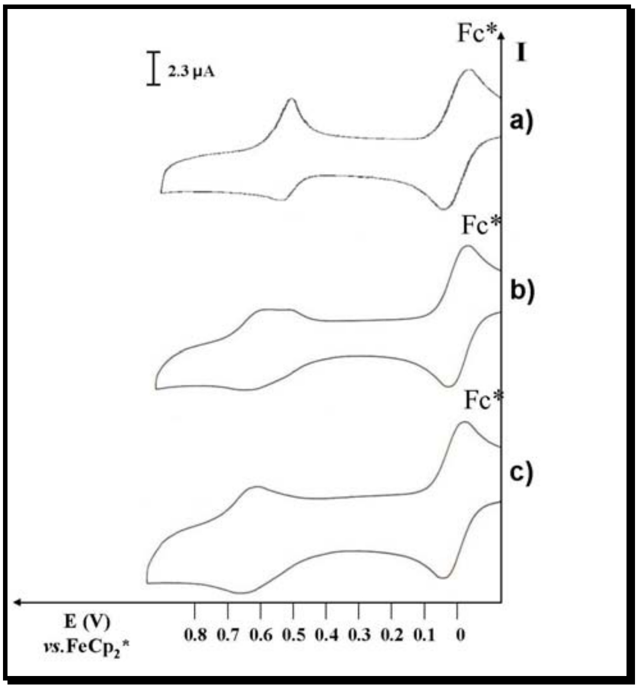


Figure 3. a) CV of $\mathbf{G_1}$ (c = 4.89×10^{-4} M) before addition $Pd(OAc)_2$; b) CV of $\mathbf{G_1}$ during titration of $Pd(OAc)_2$ (0.6 equiv. *per* triazole); c) CV of $\mathbf{G_1}$ at the end of titration of $Pd(OAc)_2$ (1 equiv. *per* triazole).

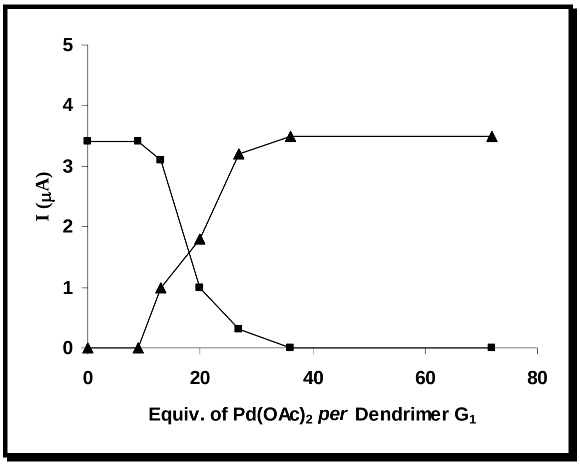


Figure 4. Titration of $Pd(OAc)_2$ with $\mathbf{G_1}$ (c = 4.89×10^{-4} M). Decrease of the intensity of the initial CV wave (■) and increase of the new CV wave (▲) vs the number of equiv. of $Pd(OAc)_2$ added per Dendrimer $\mathbf{G_1}$.

Titration of $Pd(OAc)_2$ with poly-1,2,3-triazolylferrocenyl dendrimer G_2

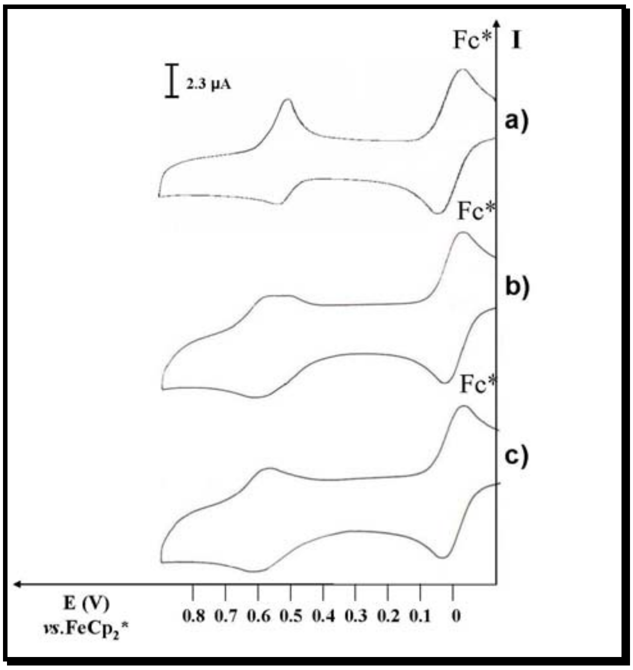


Figure 5. a) CV of $\mathbf{G_2}$ (c = 1.63×10^{-5} M) before addition $Pd(OAc)_2$; b) CV of $\mathbf{G_2}$ during titration of $Pd(OAc)_2$ (0.65 equiv. *per* triazole); c) CV of $\mathbf{G_2}$ at the end of titration of $Pd(OAc)_2$ (1 equiv. *per* triazole).

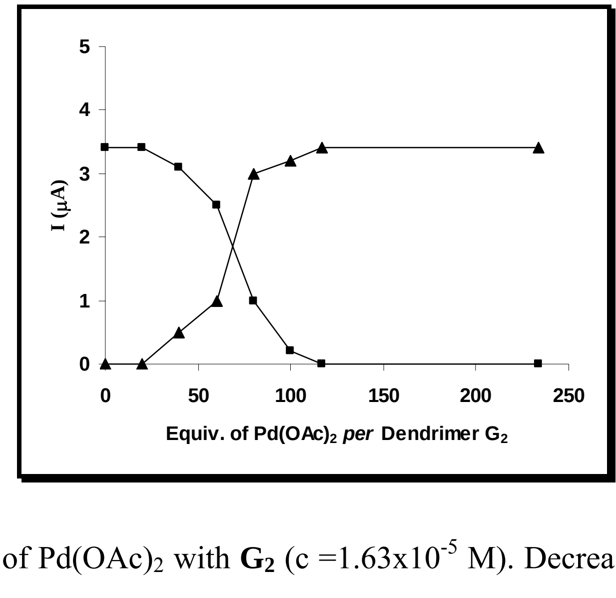


Figure 6. Titration of $Pd(OAc)_2$ with $\mathbf{G_2}$ (c =1.63×10^{-5} M). Decrease of the intensity of the initial CV wave (■) and increase of the new CV wave (▲) vs the number of equiv. of $Pd(OAc)_2$ added per Dendrimer $\mathbf{G_2}$.

UV/Vis. spectra

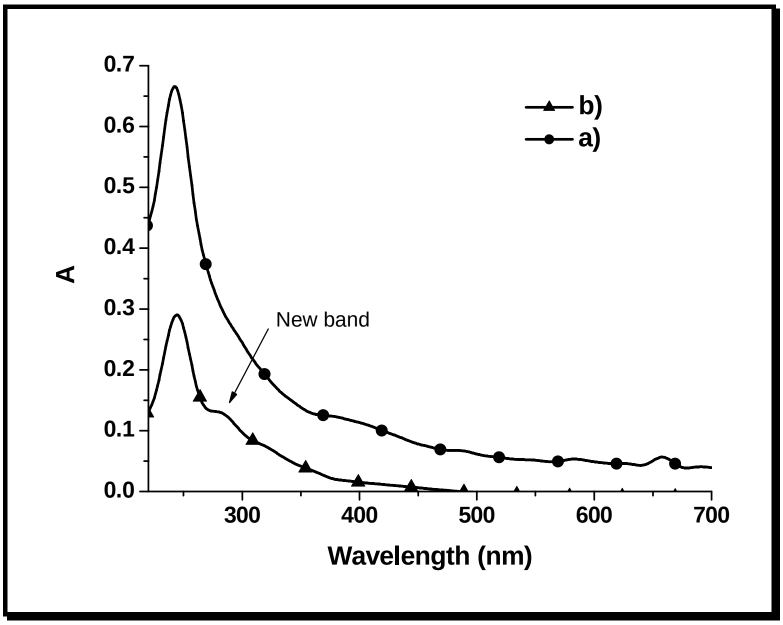


Figure 7. a) UV/Vis spectrum of a freshly prepared 7.43x10^{-5} M solution of Pd(OAc)$_2$ in CHCl$_3$/MeOH (2:1); b) Uv/visible spectra of a solution of G$_0$ (8.26x10^{-6} M) and 9 eq. of Pd(OAc)$_2$ (7.43x10^{-5} M) in CHCl$_3$/MeOH (2:1) after 30 min (using a 7.43x10^{-5} M solution of Pd(OAc)$_2$ in CHCl$_3$/MeOH (2:1) as blank), after 16h a similar spectra was obtained.

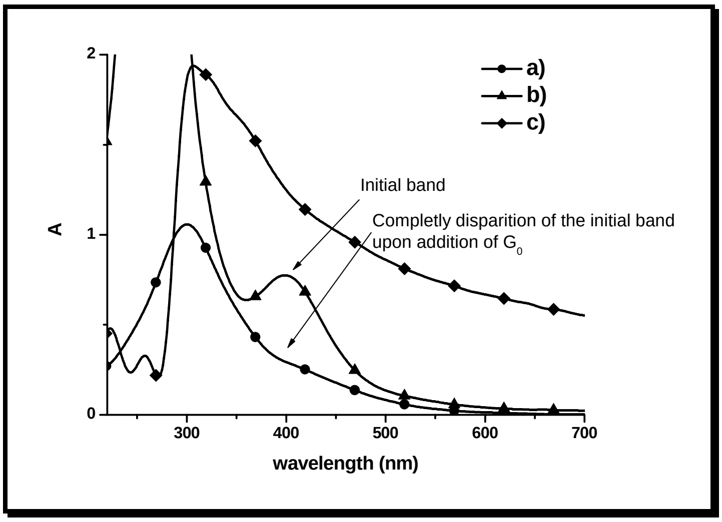


Figure 8. a) UV/Vis. spectrum of a freshly prepared 2.97x10^{-3} M solution of Pd(OAc)$_2$ in CHCl$_3$/MeOH (2:1); b) UV/Vis. spectrum of a solution of G$_0$ (9.78x10^{-5} M) and 9 eq. of Pd(OAc)$_2$ (8.80x10^{-4} M) in CHCl$_3$/MeOH (2:1) after 30 min (using a 9.78x10^{-5} M solution of dendrimer in CHCl$_3$/MeOH (2:1) as blank); c) UV/Vis. spectrum of the PdNP obtained by reduction with NaBH$_4$ (similar spectra was obtained using MeOH as reductant).

Transmission Electron Microscopy (TEM) data

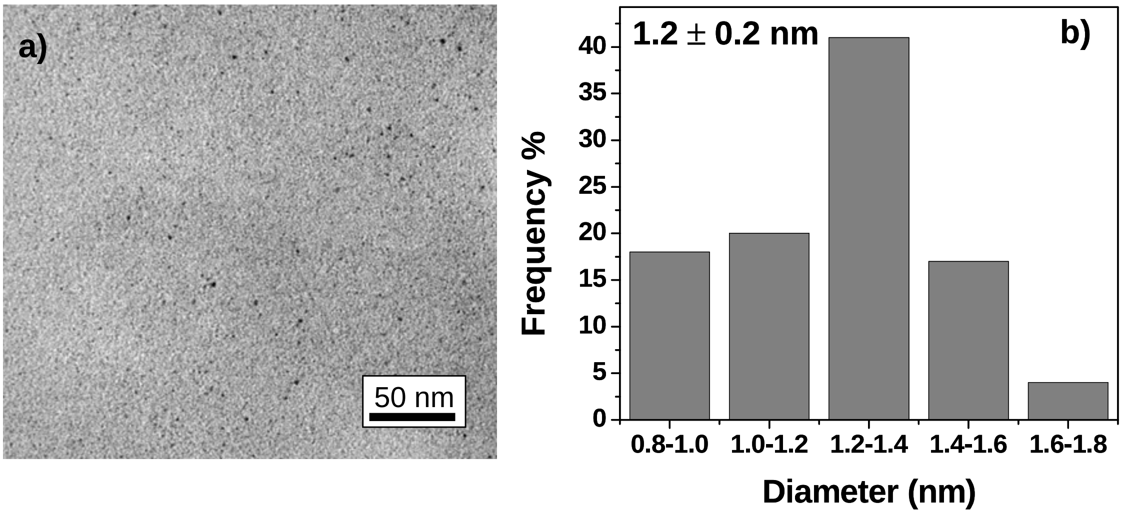


Figure 9. DEN-G_0/method 1: a) TEM image and b) size distribution.

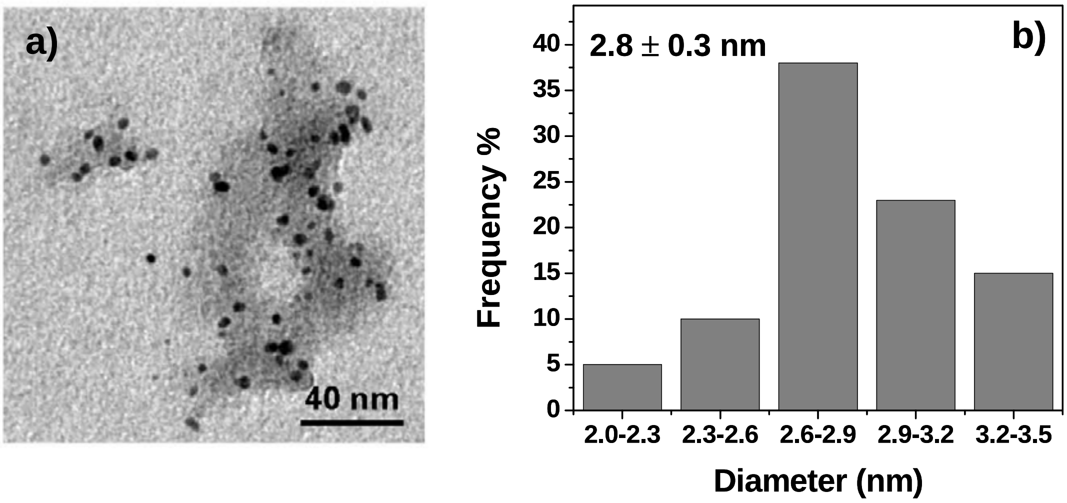


Figure 10. DEN-G_0/method 2: a) TEM image and b) size distribution.

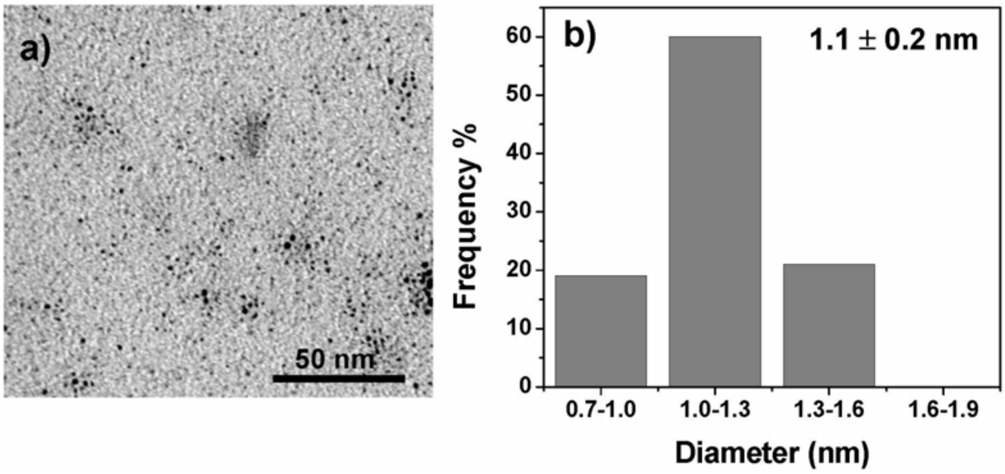


Figure 11. DEN-G_1/method 1: a) TEM image and b) size distribution.

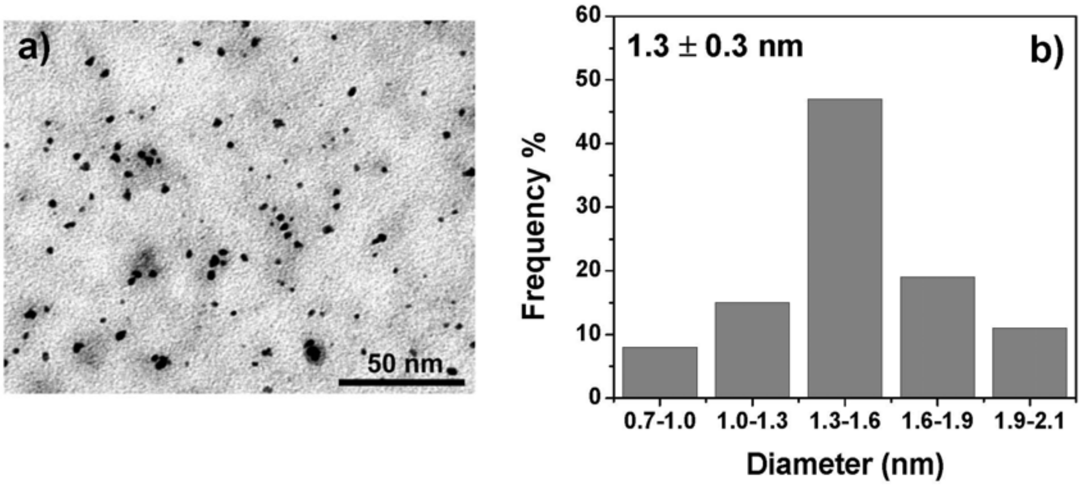


Figure 12. DEN-G_1/method 2: a) TEM image and b) size distribution.

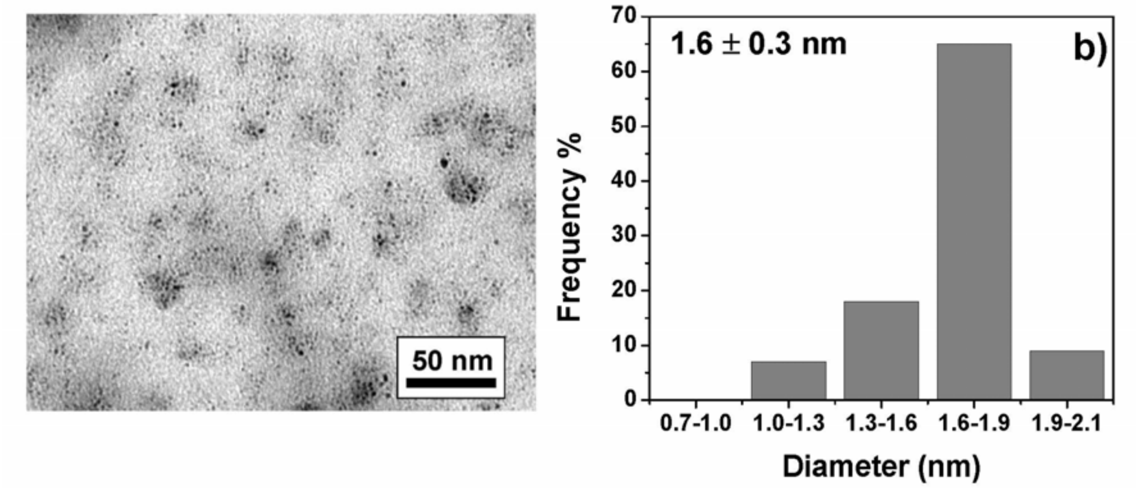


Figure 13. DEN-G_2/method 1: a) TEM image and b) size distribution.

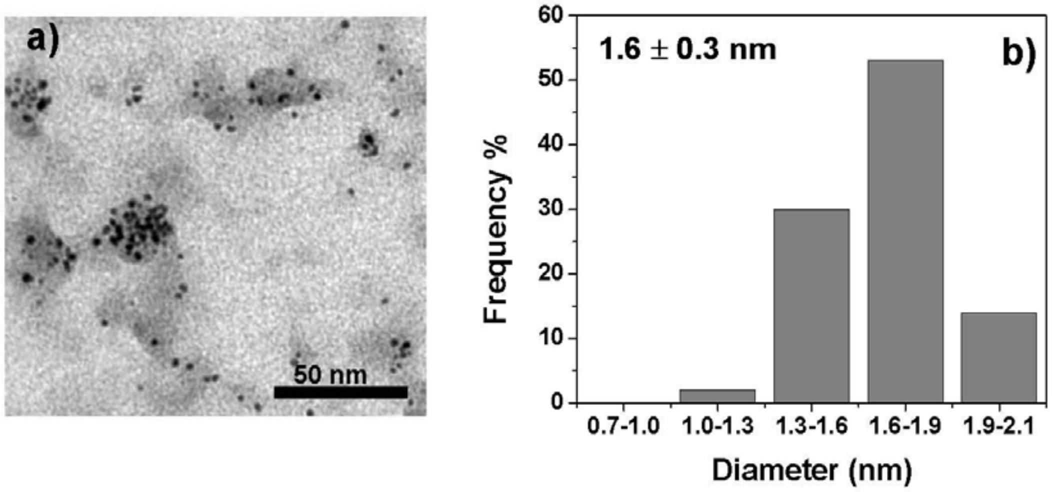


Figure 14. DEN-G_2/method 2: a) TEM image and b) size distribution.

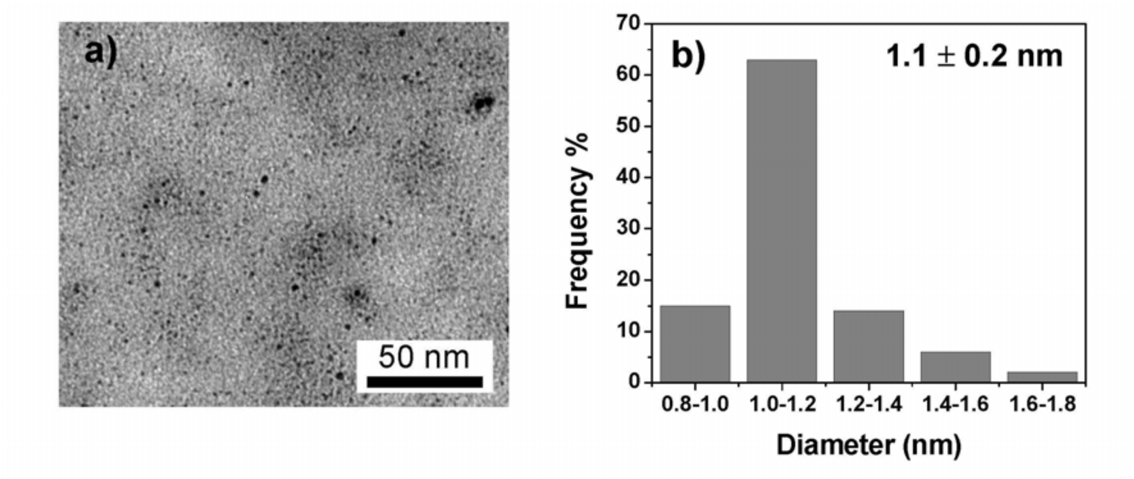


Figure 15. DEN-G_2-36/method 1: a) TEM image and b) size distribution.

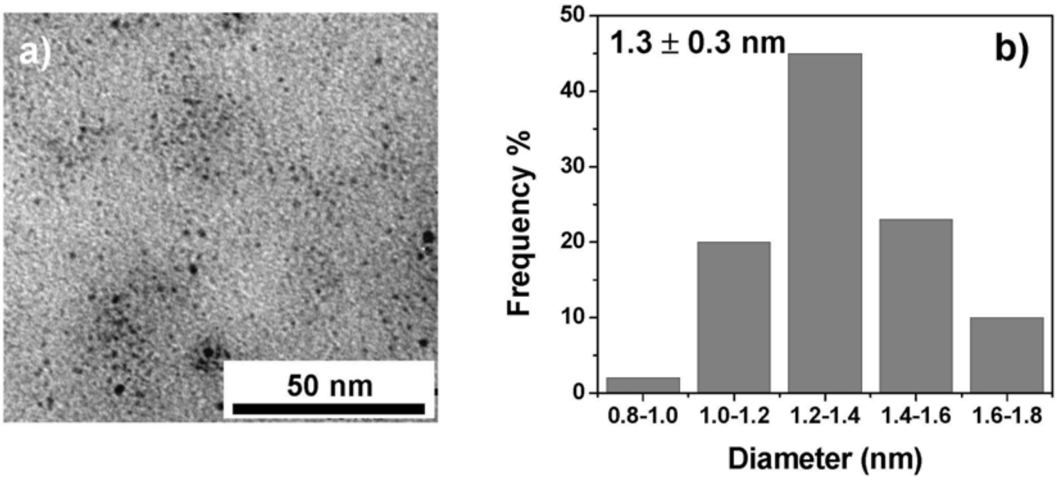


Figure 16. DEN-G_2-36/method 2: a) TEM image and b) size distribution.

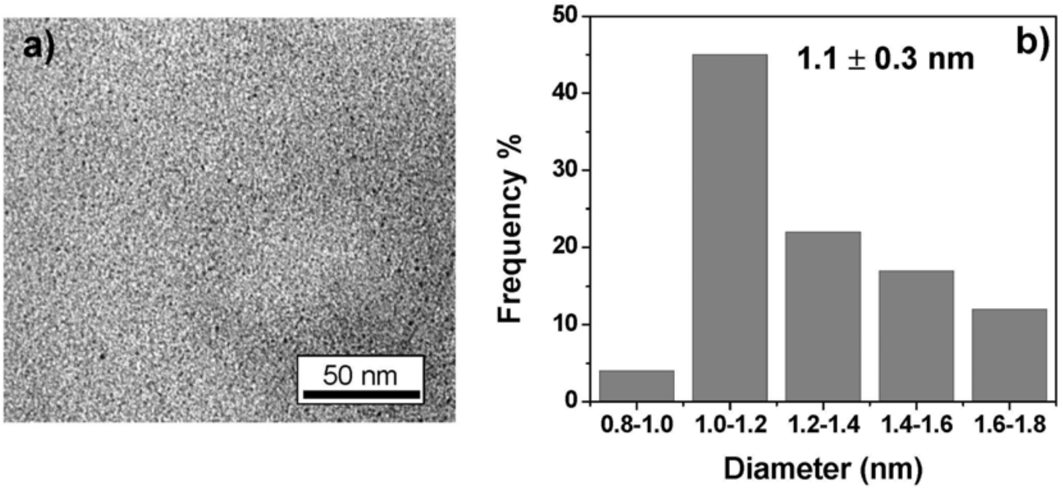


Figure 17. DEN-PAMAM/method 1: a) TEM image and b) size distribution.

NMR Spectra of $Pd(OAc)_2$ complexation

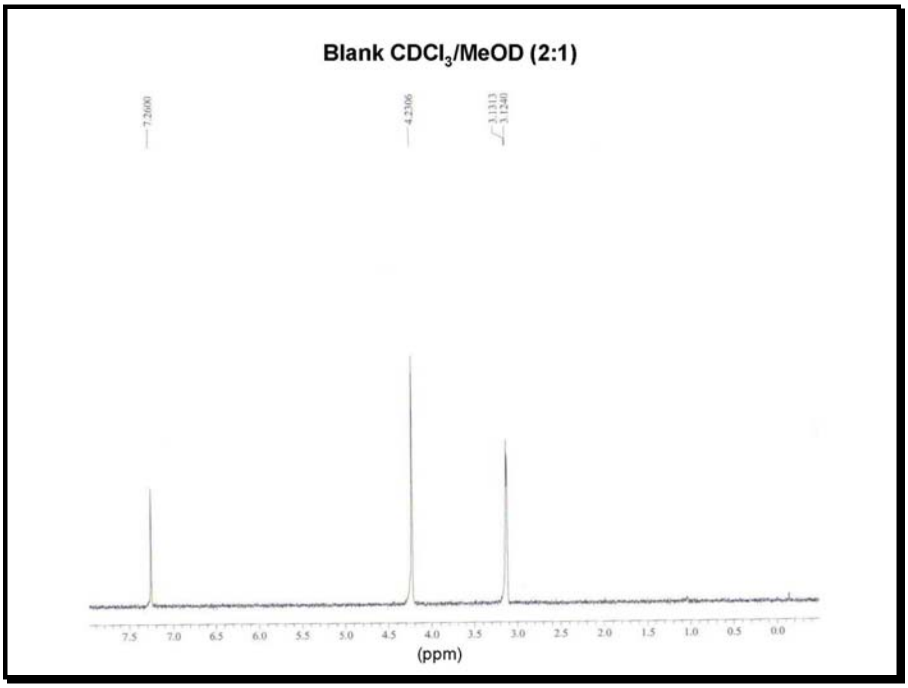


Figure 18. ^1H NMR spectrum of the blank $CDCl_3$/MeOD (2:1).

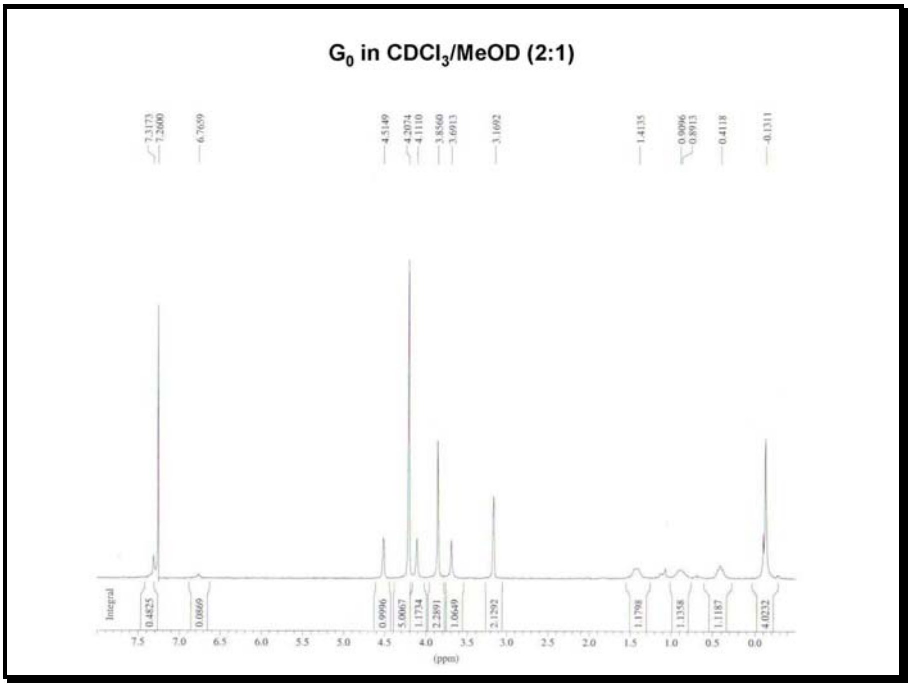


Figure 19. ^1H NMR spectrum of $\mathbf{G_0}$ in $CDCl_3$/MeOD (2:1).

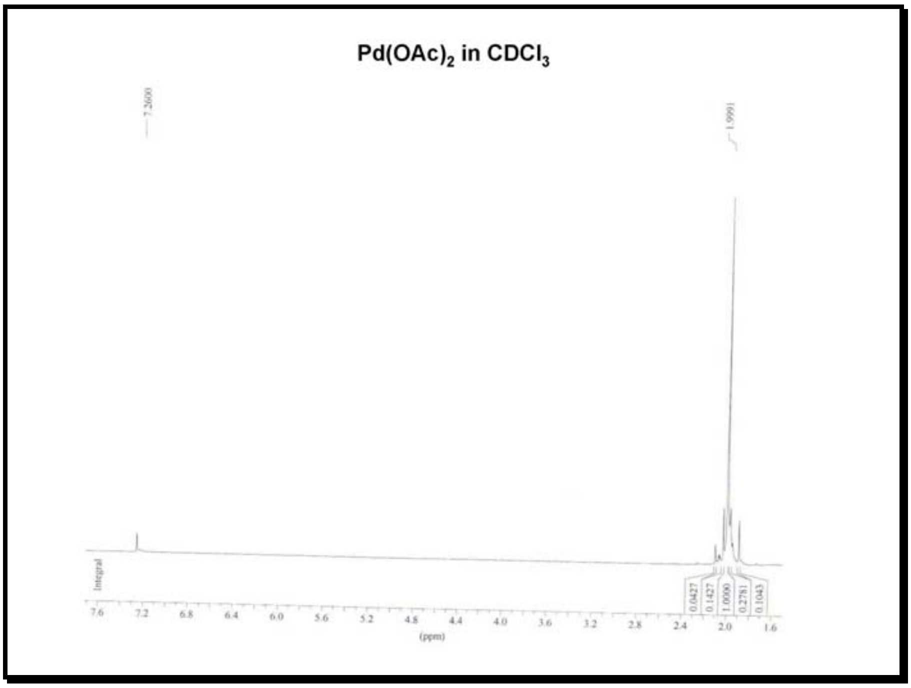


Figure 20. ^{1}H NMR spectrum of $Pd(OAc)_2$ in $CDCl_3$.

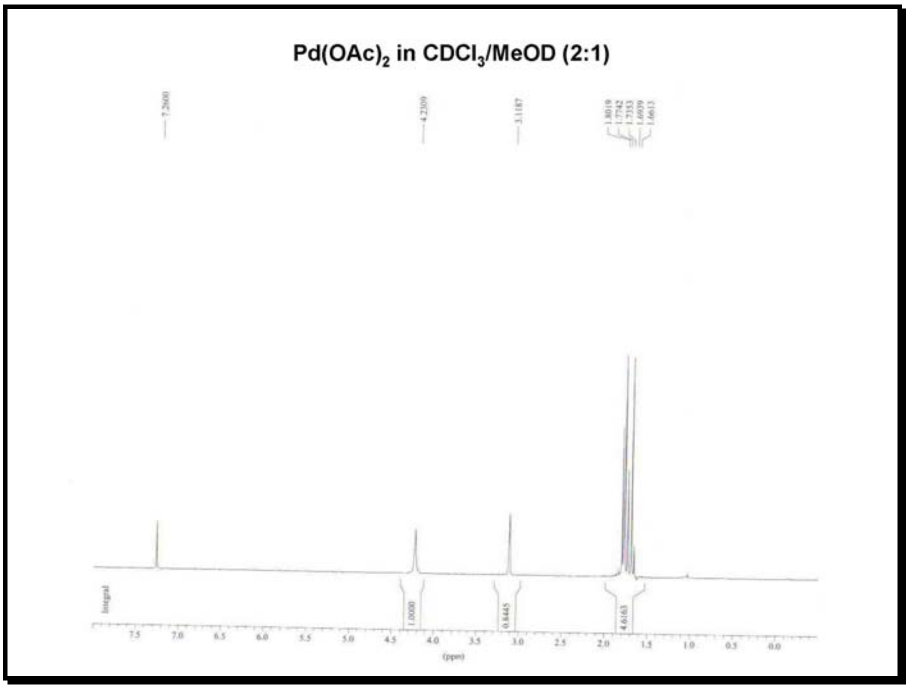


Figure 21. ^{1}H NMR spectrum of $Pd(OAc)_2$ in $CDCl_3$/MeOD (2:1) after 5 min.

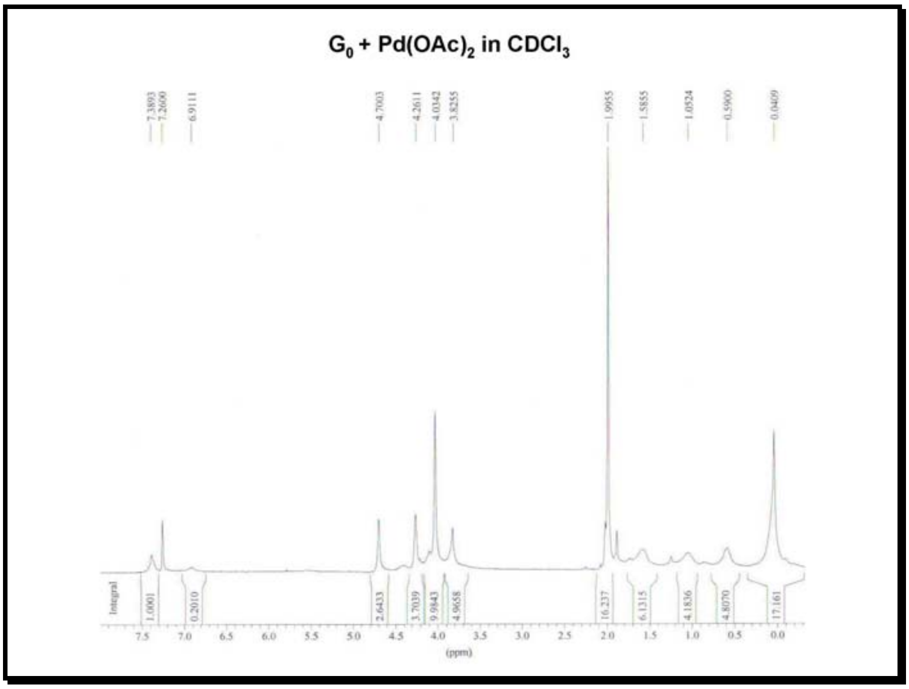


Figure 22. ^1H NMR spectrum of $\mathbf{G_0}$ and 9 eq. of $Pd(OAc)_2$ in $CDCl_3$; no interaction is observed.

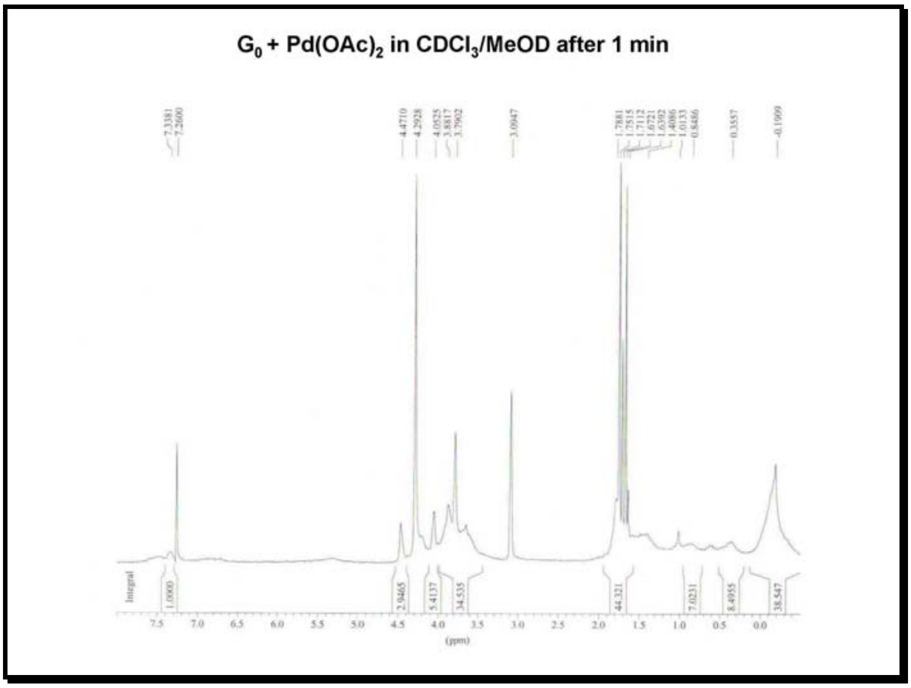


Figure 23. ^1H NMR spectrum of G_0 and 9 eq. of $Pd(OAc)_2$ in $CDCl_3$/MeOD (2:1) after 1 min.

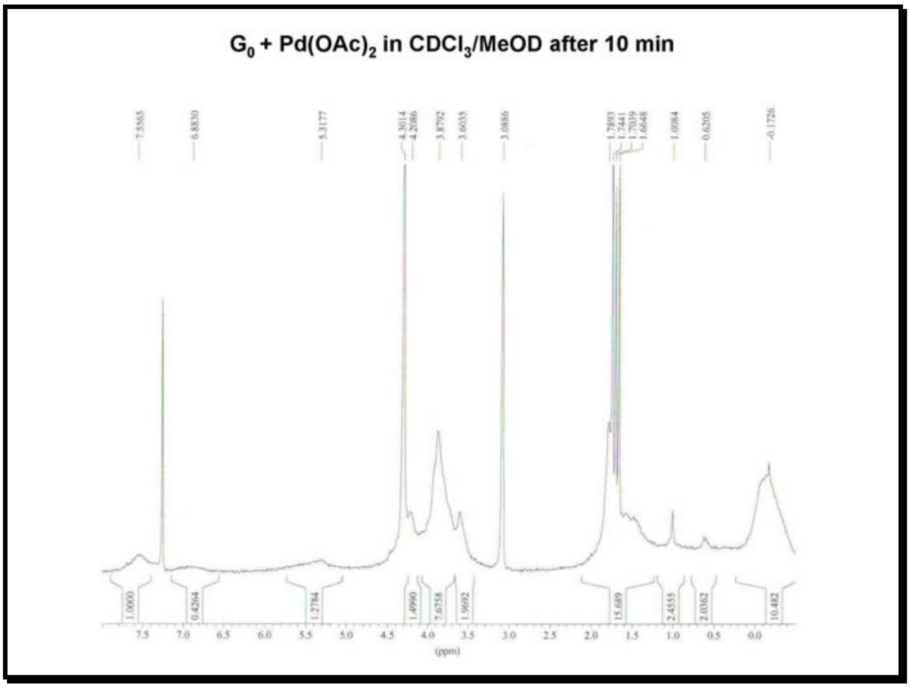


Figure 24. ^{1}H NMR spectrum of G_0 and 9 eq. of $Pd(OAc)_2$ in $CDCl_3$/MeOD (2:1) after 10 min.

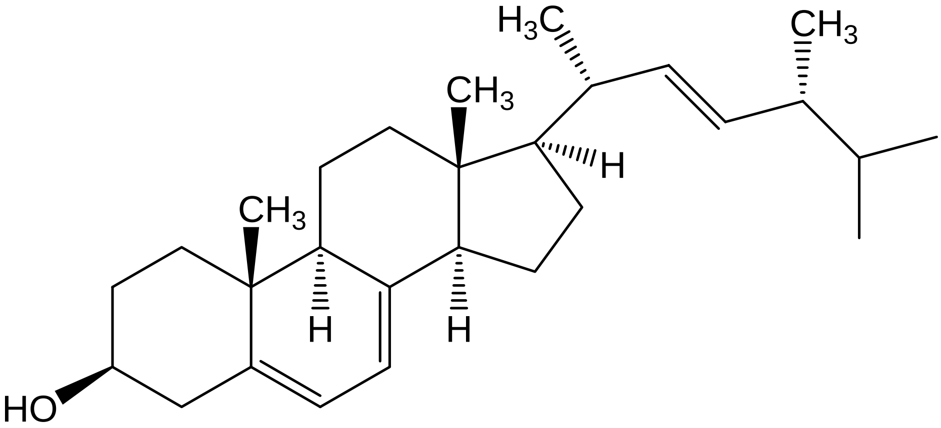
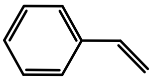
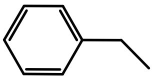
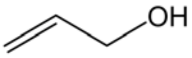
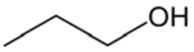
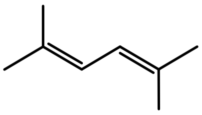
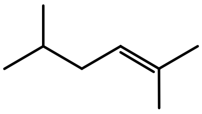
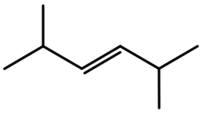
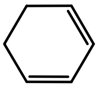
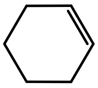
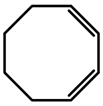
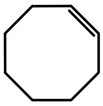
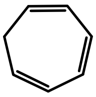
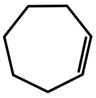
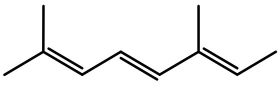
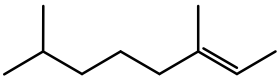
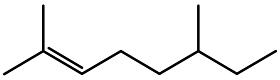
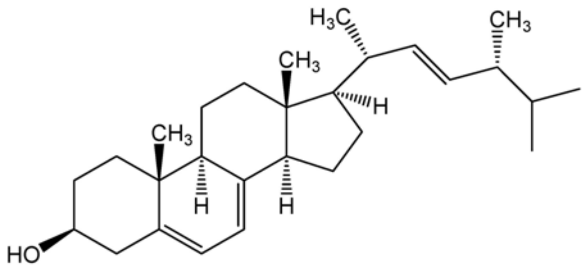


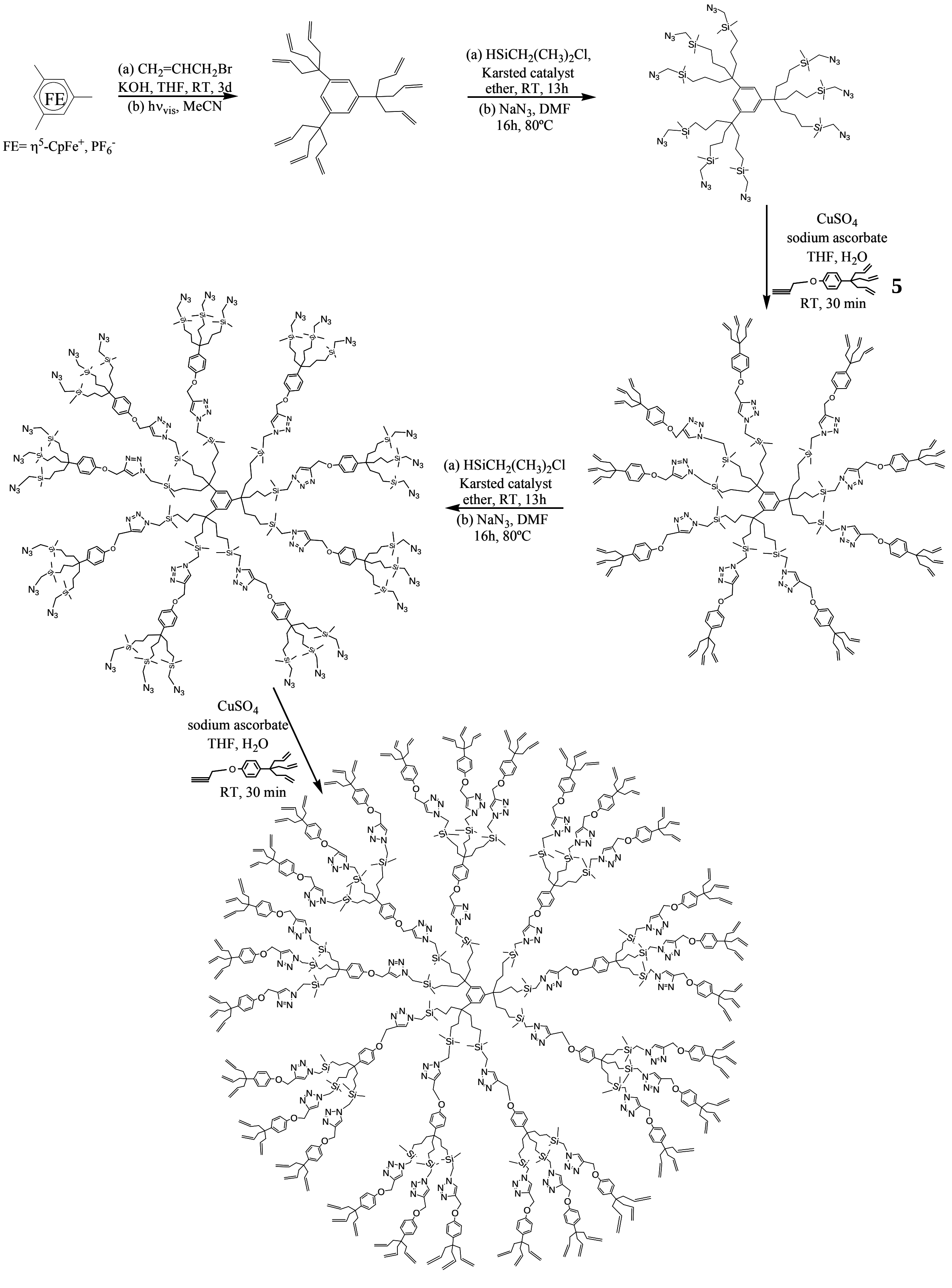
Figure 25. Chemical structure of Ergosterol.

Table 2. Hydrogenation of olefins catalyzed by DEN-G_1a/method 2.

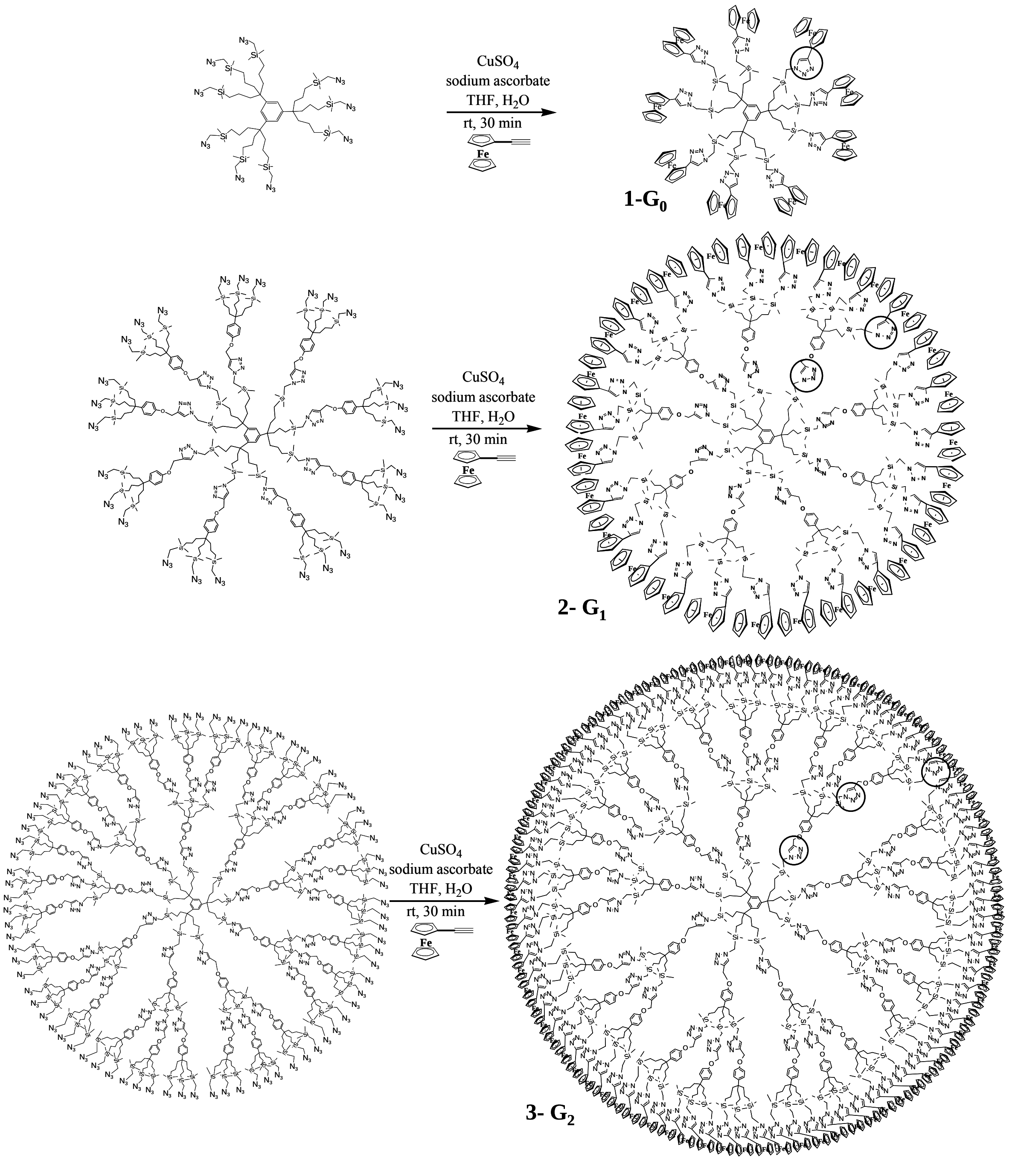
Substrate	Products[a] (yield)	TOF[b]
	 (100%)	1 620
	 (100%)	1 160
	 (43%)	1 800
	 (57%)	2 400
	 (78%)	810
	 (22%)	230
	 (100%)	1 150
	 (100%)	530
	 (100%)	130
	 	480[c]
 Ergosterol[d]	No hydrogenation	-

[a] Reactions were performed at 25ºC/1 atm H_2 and followed by GPC, in the case of styrene and by NMR in the other cases. [b] TOF values were determined on basis of the yield of formation of the final product. [c] The NMR data do not allow to determinate the relative quantities of the two isomers formed. [d] Ergosterol was left under hydrogenation conditions during four days.

Synthesis of dendrimers[E.S.I.2]



Scheme 1. Synthesis of an 81-allyl dendrimer by “Click Chemistry”.



1-G$_0$

2- G$_1$

3- G$_2$

Scheme 2. Synthesis of the 1,2,3-triazolylferrocenyl dendrimers by "Click Chemistry".

General procedure for "Click" reactions: The azide-dendrimer (1 equiv.) and the alkyne (1.5 equiv. *per* branch) were dissolved in tetrahydrofuran (THF) and water was added (1:1 THF/water). At 0°C, the $CuSO_4$ was added (1 equiv. *per* branch, 1M aqueous solution), followed by the dropwise addition of a freshly prepared solution of sodium ascorbate (2 equiv. *per* branch, 1M aqueous solution). The solution was allowed to stir for 30 min. at room temperature. After removing THF under vacuum, dichloromethane and aqueous solution of ammonia were added. The mixture was allowed to stir for 10 min in order to remove all the Cu^I trapped inside the dendrimer as $Cu(NH_3)_6^+$. The organic phase was washed twice with water, filtrated under celite and solvent removed under vacuum. The product was washed with pentane in order to remove the excess of alkyne and precipitated using dichloromethane/pentane. Organic dendrimers were obtained as colorless waxy products and ferrocenyl dendrimers were obtained as orange waxy products usually in high yields in both cases. For details of all experimental procedures, characterization data of all products, mass spectra, ^{1}H RMN spectra, cyclic voltammetry conditions and voltammograms of titrations please see reference [E.S.I.2].

[E.S.I.2] C. Ornelas, J. Ruiz Aranzaes, E. Cloutet, S. Alves, D. Astruc, *Angew. Chem., Int. Ed. Engl.* **2007,** *46*, 872.