Supporting information

Easy preparation of small crystalline Pd_2Sn nanoparticles in solution at room temperature

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Table of contents

Characterization of the Pd and Pd_2Sn NPs

Transmission Electron Microscopy (TEM)

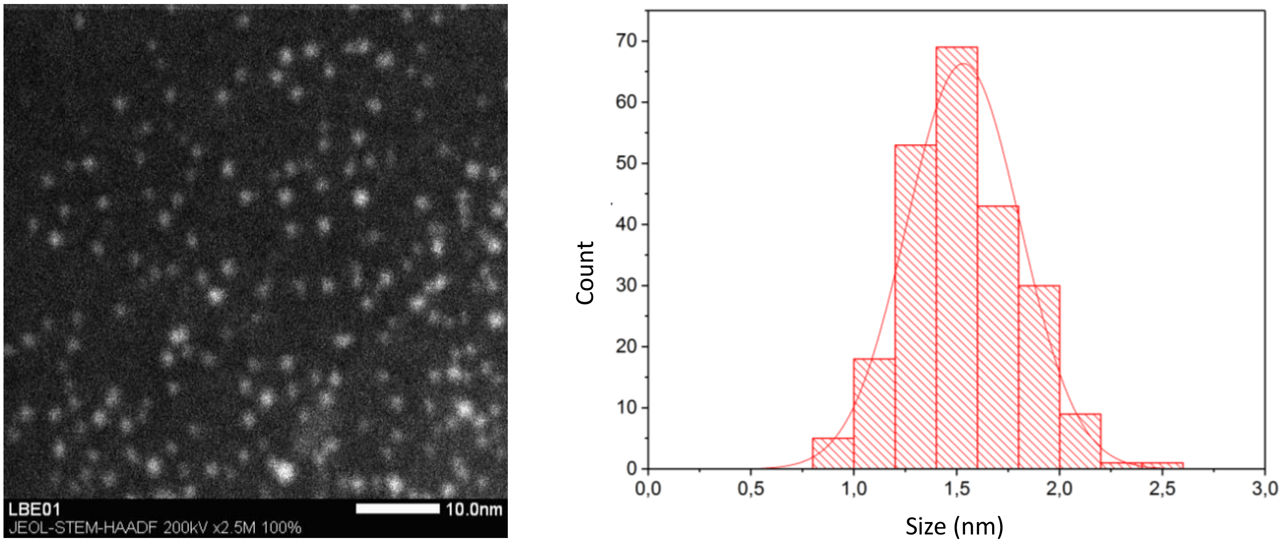


Figure S1 –Left: STEM-HAADF image (on a copper grid with a carbon lacey) of 1.5 ± 0.3 nm sized palladium nanoparticles synthesized at room temperature with 1.5 equiv. of silane under 4 bars of H_2 in toluene.
Right: size distribution of these nanoparticles with the corresponding normal distribution curve.

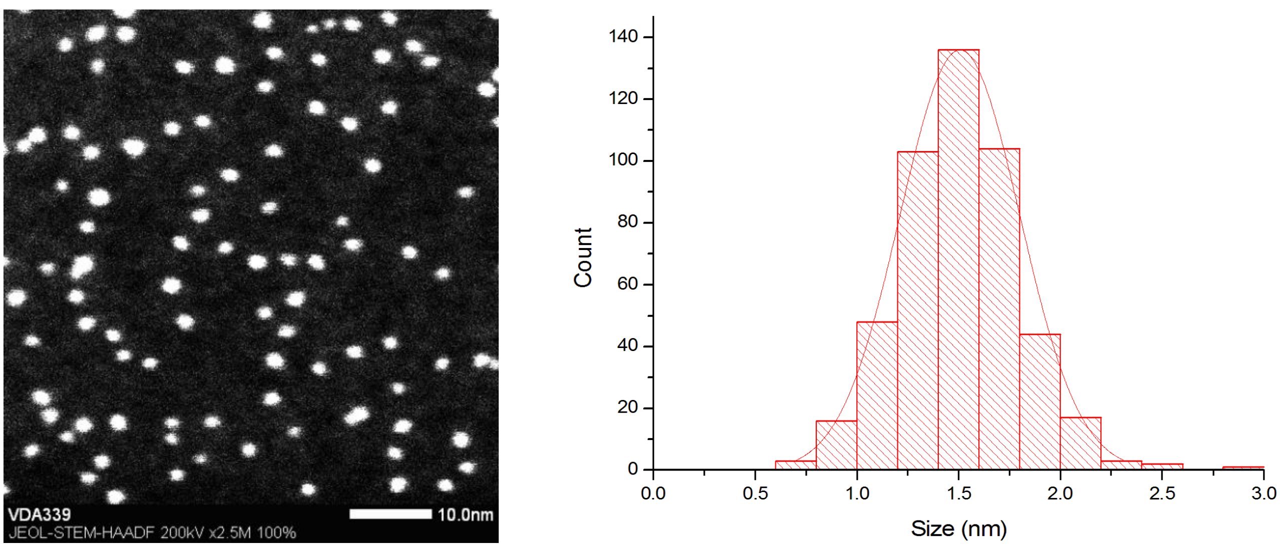


Figure S2 – Left: STEM-HAADF image (on a copper grid with a carbon lacey) of 1.5 ± 0.3 nm sized palladium nanoparticles synthesized at room temperature with 1.5 equiv. of silane under 4 bars of H_2 in THF.
Right: size distribution of these nanoparticles with the corresponding normal distribution curve.

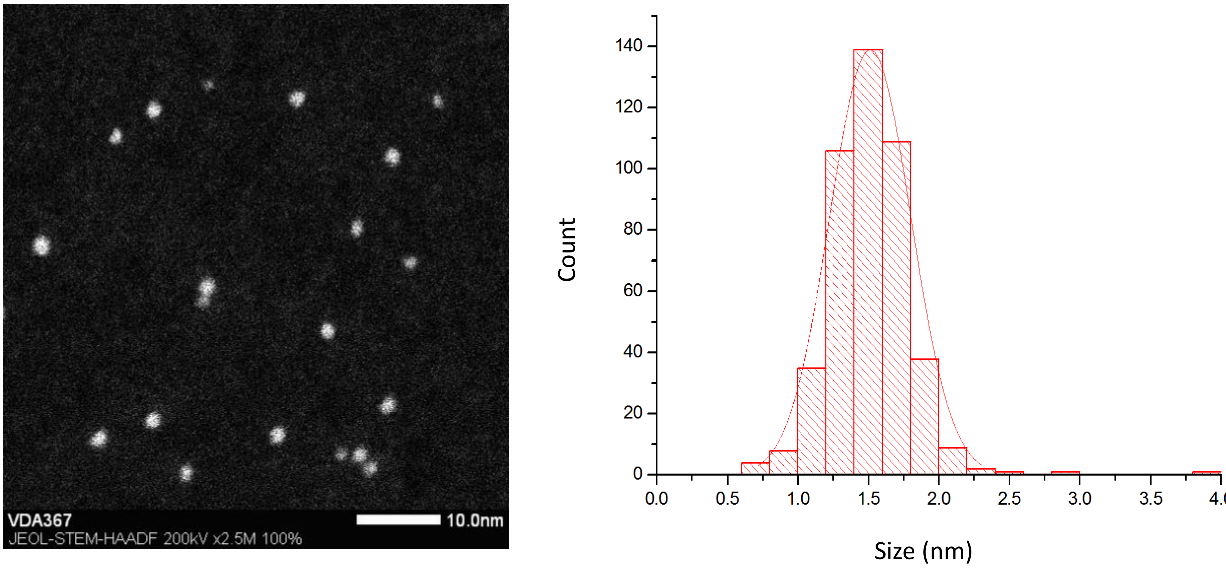


Figure S3 – Left: STEM-HAADF image (on a copper grid with a carbon lacey) of 1.5 ± 0.3 nm sized palladium nanoparticles synthesized at room temperature with 2 equiv. of silane under 4 bars of H_2 in toluene.
Right: size distribution of these nanoparticles with the corresponding normal distribution curve.

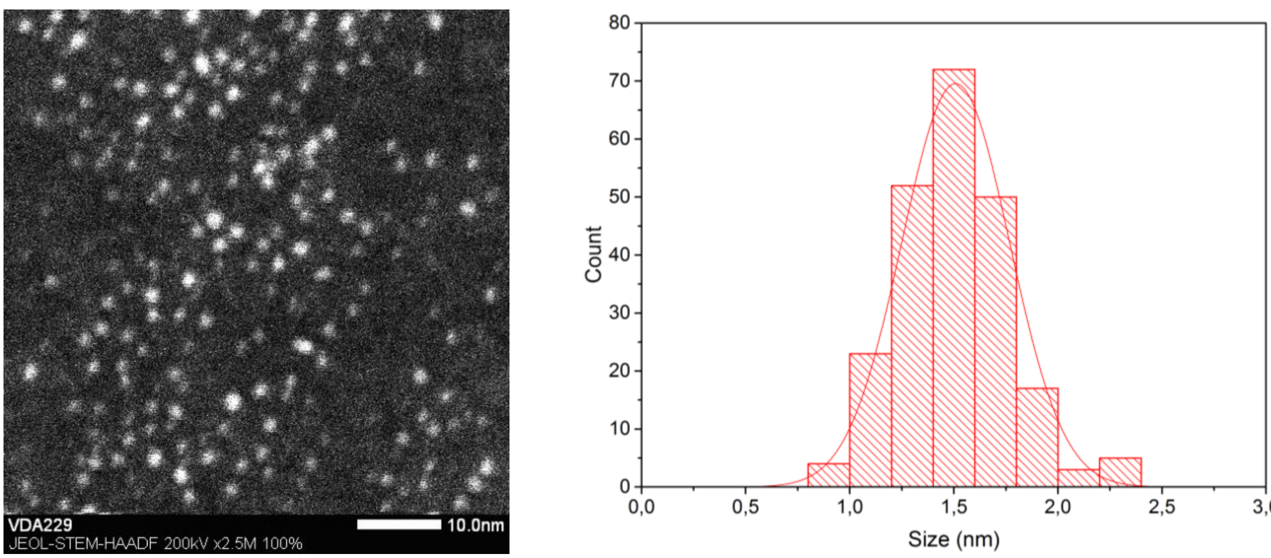
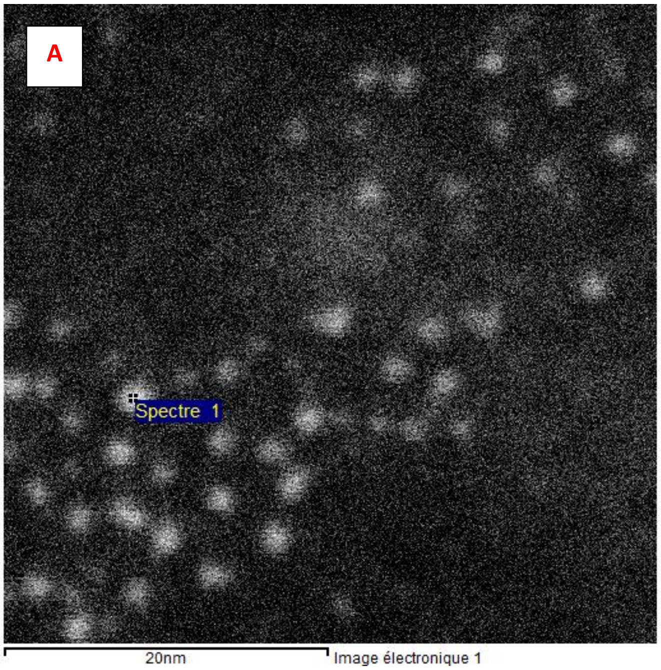
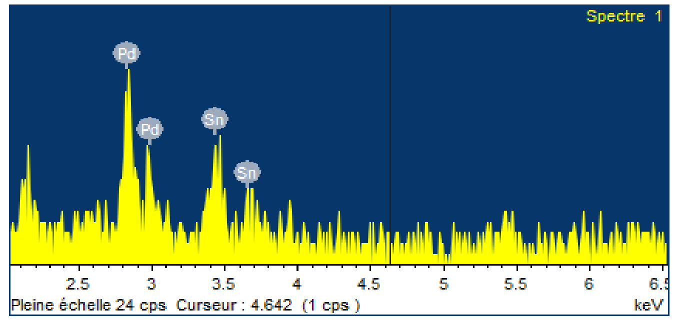
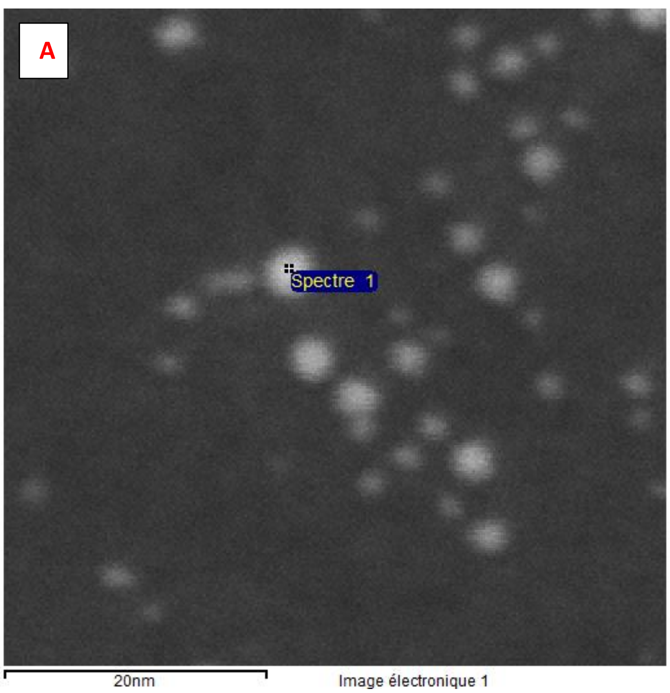


Figure S4 – Left: STEM-HAADF image (on a copper grid with a carbon lacey) of 1.5 ± 0.3 nm sized palladium-tin nanoparticles synthesized at room temperature with 2 equiv. of tin precursor under 4 bars of H_2 in THF. Right: size distribution of these nanoparticles with the corresponding normal distribution curve.

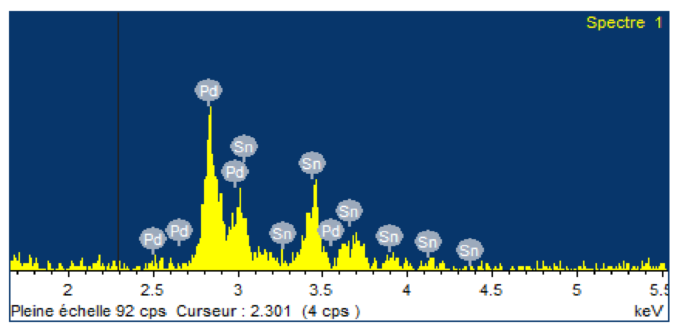


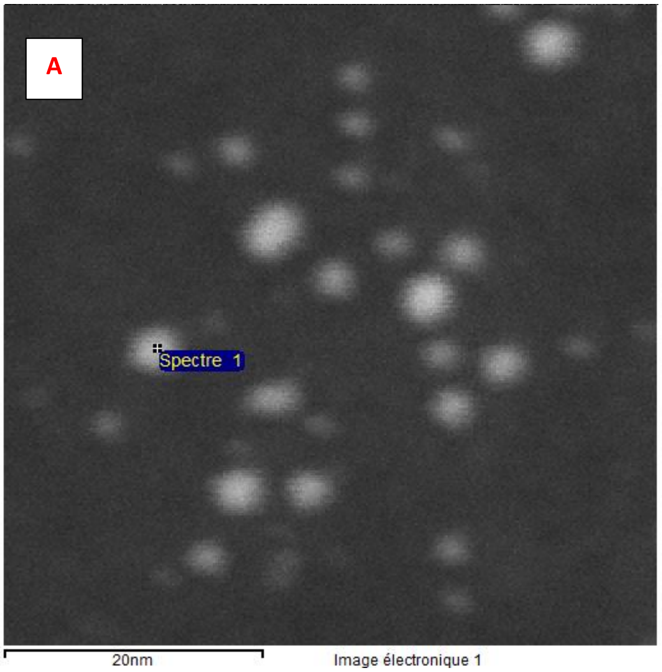
Element	%Mass	%Atomic
Pd L	60.82	63.39
Sn L	39.18	36.61
Total	100.00	



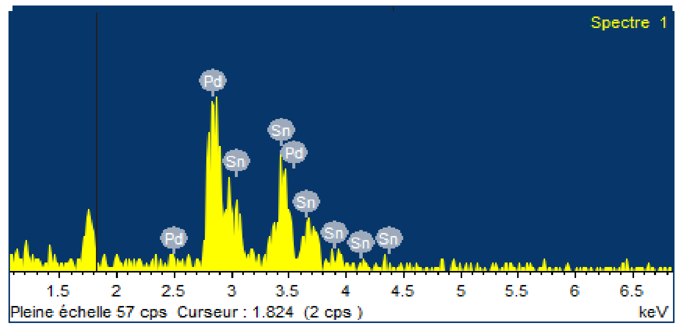


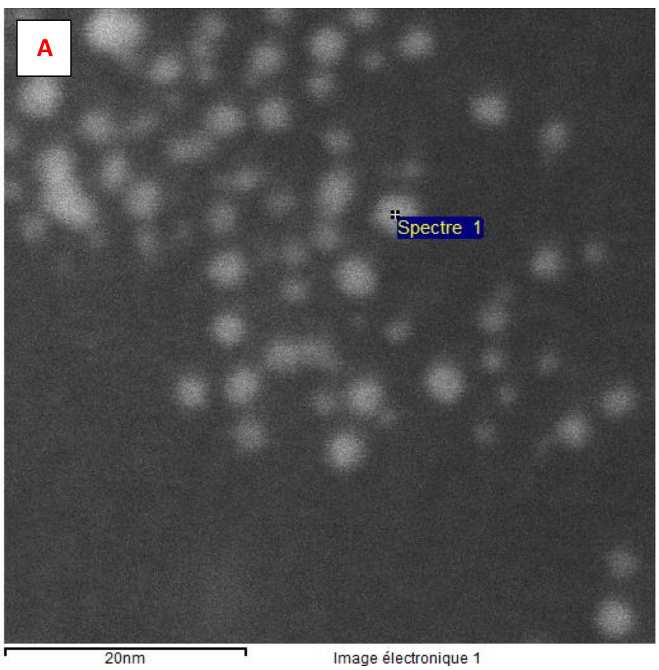
Element	%Mass	%Atomic
Pd L	63.67	66.16
Sn L	36.33	33.84
Total	100.00	



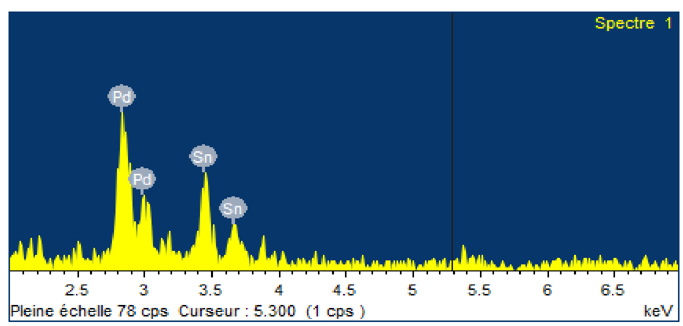


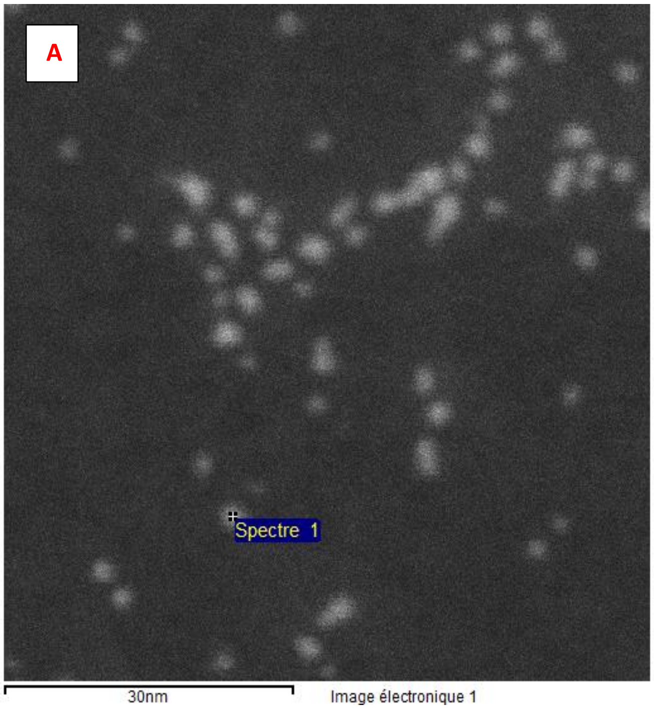
Element	%Mass	%Atomic
Pd L	60.69	63.27
Sn L	39.31	36.73
Total	100.00	



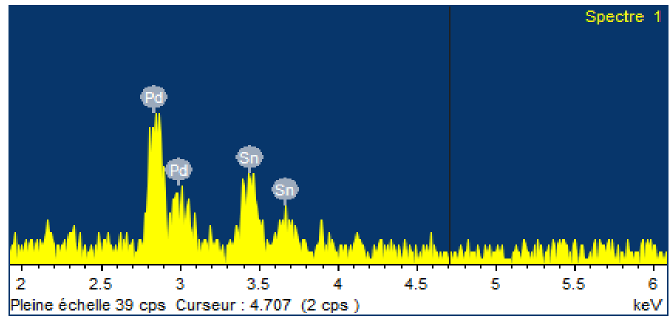


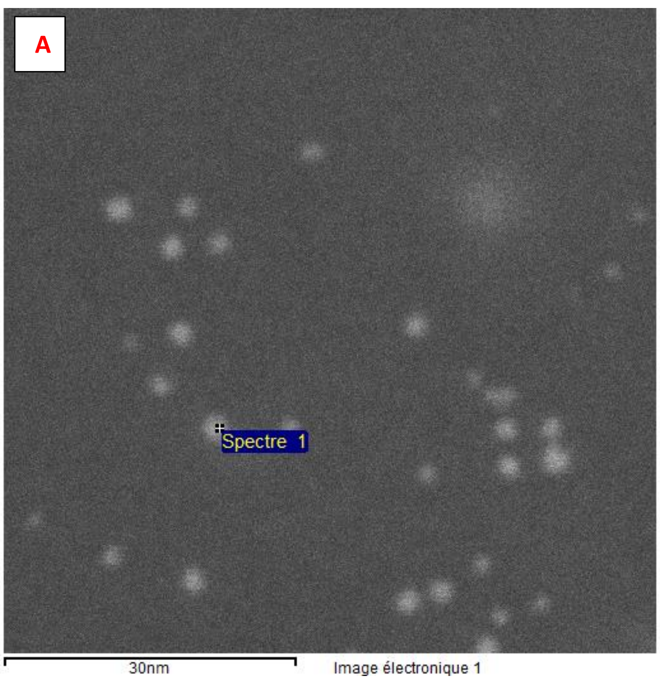
Element	%Mass	%Atomic
Pd L	61.13	63.69
Sn L	38.87	36.31
Total	100.00	



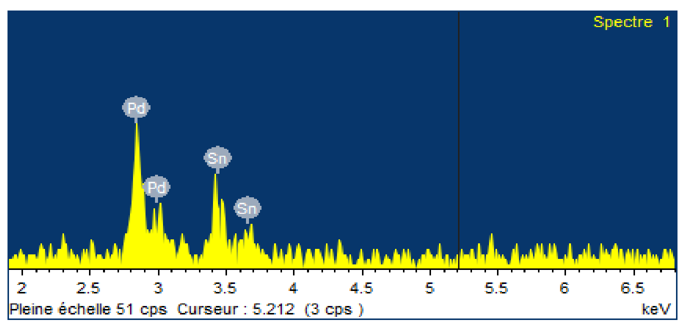


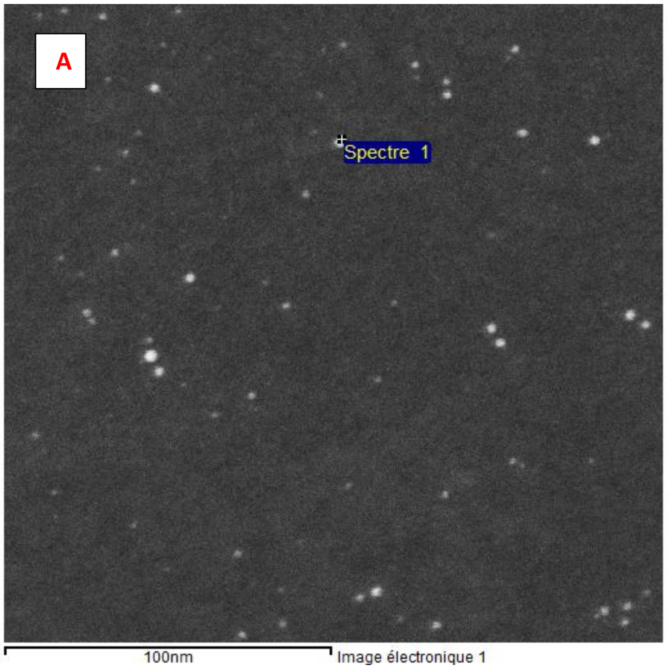
Element	%Mass	%Atomic
Pd L	62.85	65.37
Sn L	37.15	34.63
Total	100.00	



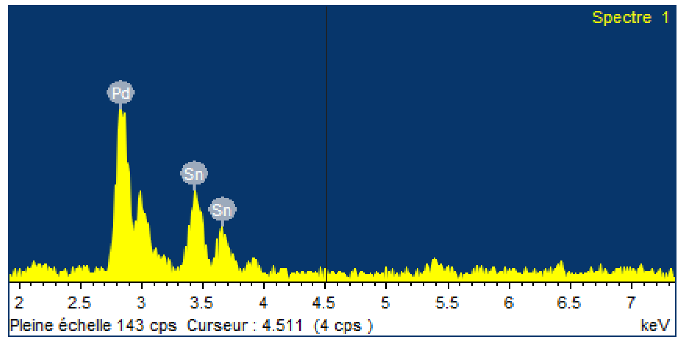


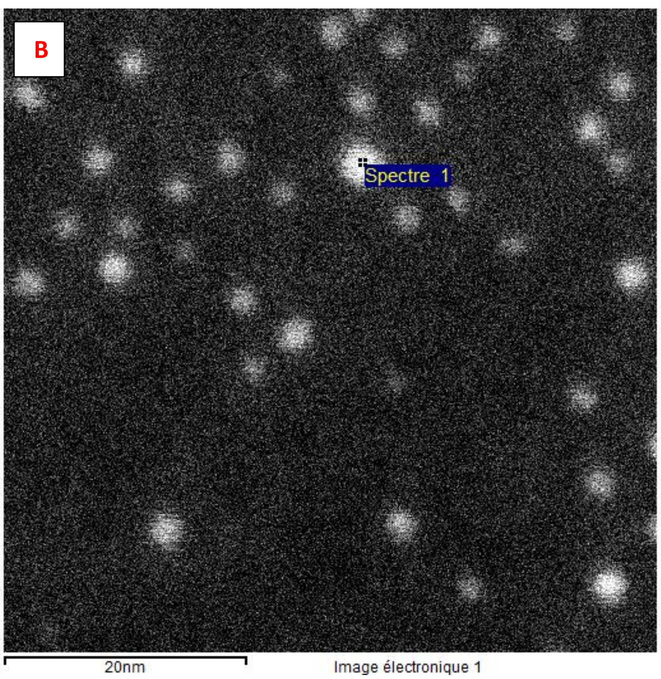
Element	%Mass	%Atomic
Pd L	64.22	66.69
Sn L	35.78	33.31
Total	100.00	





Element	%Mass	%Atomic
Pd L	64.54	67.00
Sn L	35.46	33.00
Total	100.00	





Element	%Mass	%Atomic
Pd L	96.99	89.48
Si K	3.01	10.52
Total	100.00	

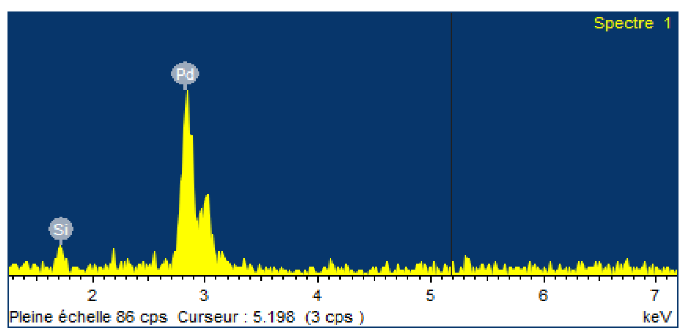


Figure S5 – A) STEM-HAADF-EDS of the palladium-tin nanoparticles (on a copper grid with a carbon lacey) synthesized at room temperature with 2 equiv. of tin precursor under 4 bars of H_2 in THF - B) STEM-HAADF-EDS of the palladium nanoparticles (on a copper grid with a carbon lacey) synthesized at room temperature with 2 equiv. of silane under 4 bars of H_2 in THF.

Crystalline phase determination

		Experimental	Theoretical hexagonal Pd
D (nm) (h,k,l)	**N°1**	0.241 (1,0,0)	0.241(1,0,0)
	N°2	0.229 (0,1,1)	0.227 (0,1,1)
	N°3	0.229 (-1,1,1)	0.227 (-1,1,1)
Angle (°)	**N°1**	0	0
	N°2	60.7	61.8
	N°3	114.6	118.1

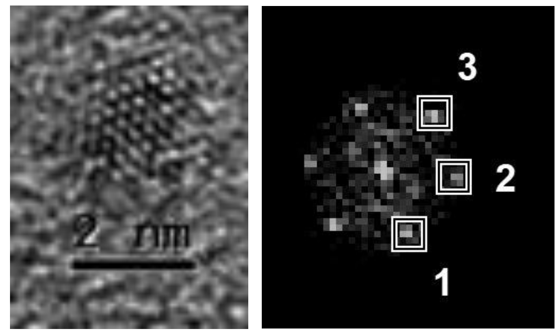
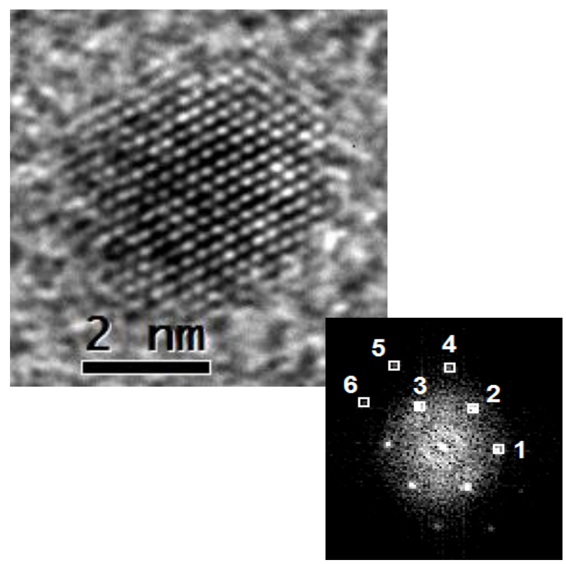
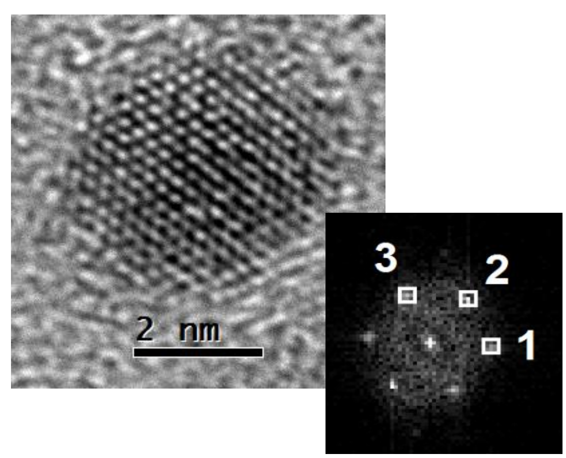


Figure S6 – HRTEM of palladium nanoparticles (on a copper grid with a carbon lacey) synthesized at room temperature with 1.5 equiv. of silane under 4 bars of H_2 with the corresponding Fourier Transform and the attributed planes and angles, compared to hexagonal Pd structure from JCPDS file n°01-072-0710.

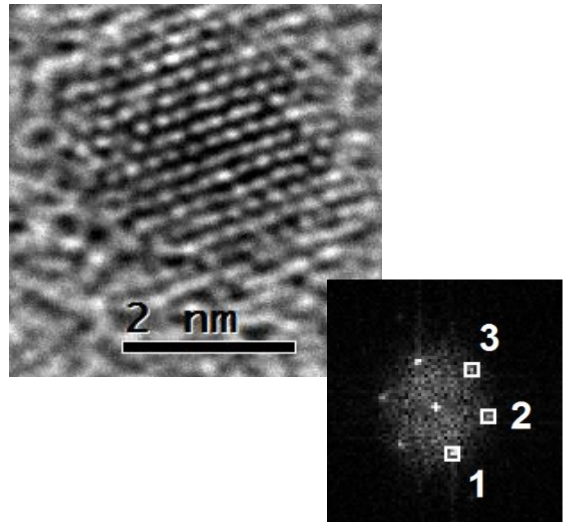
		Experimental	Theoretical Pd_2Sn alloy
D (nm) (h,k,l)	**N°1**	0.215 (0,2,0)	0.216 (0,2,0)
	N°2	0.225 (2,1,1)	0.227 (2,1,1)
	N°3	0.231 (2,-1,1)	0.227 (2,-1,1)
	N°4	0.133 (4,0,2)	0.133 (4,0,2)
	N°5	0.114 (4,-2,2)	0.113 (4,-2,2)
	N°6	0.129 (2,-3,1)	0.127 (2,-3,1)
Angle (°)	**N°1**	0	0
	N°2	58.3	58.2
	N°3	120.6	121.8
	N°4	88.9	90
	N°5	120.7	121.8
	N°6	151.0	151.7



		Experimental	Theoretical Pd_2Sn alloy
D (nm) (h,k,l)	**N°1**	0.218 (0,2,0)	0.216 (0,2,0)
	N°2	0.222 (2,1,1)	0.227 (2,1,1)
	N°3	0.241 (-2,1,-1)	0.227 (-2,1,-1)
Angle (°)	**N°1**	0	0
	N°2	56.9	58.2
	N°3	118.9	121.8



	Experimental	Theoretical Pd_2Sn alloy
D (nm) (h,k,l) N°1	0.224 (2,1,1)	0.227 (2,1,1)
N°2	0.218 (0,2,0)	0.216 (0,2,0)
N°3	0.224 (-2,1,-1)	0.227 (-2,1,-1)
Angle (°) N°1	0	0
N°2	56.9	58.2
N°3	118.9	116.5



	Experimental	Theoretical Pd_2Sn alloy
D (nm) (h,k,l) N°1	0.210 (0,2,0)	0.216 (0,2,0)
N°2	0.229 (2,1,1)	0.227 (2,1,1)
N°3	0.233 (2,-1,1)	0.227 (2,-1,1)
N°4	0.123 (2,3,1)	0.127 (2,3,1)
N°5	0.140 (4,0,2)	0.133 (4,0,2)
N°6	0.123 (2,-3,1)	0.127 (2,-3,1)
Angle (°) N°1	0	0
N°2	54.6	58.2
N°3	123.6	121.8
N°4	25.7	28.3
N°5	89	90
N°6	153.7	151.7

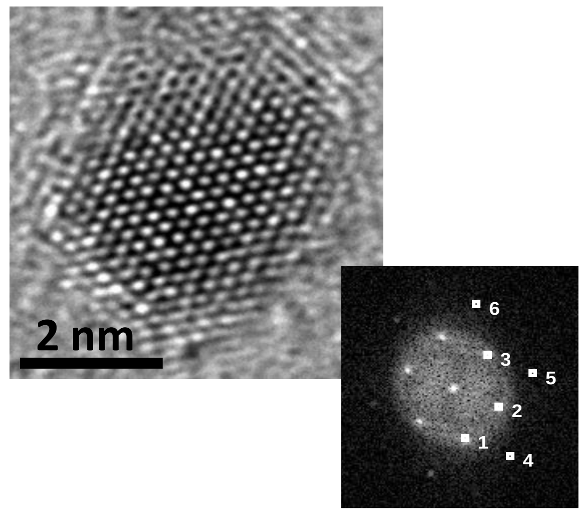


Figure S7 – HRTEM of palladium-tin nanoparticles (on a copper grid with a carbon lacey) synthesized at room temperature with 2 equiv. of tin precursor under 4 bars of H_2 with the corresponding Fourier Transform and the attributed planes and angles compared to orthorhombic Pd_2Sn structure from JCPDS file n°04-004-2280.

XPS

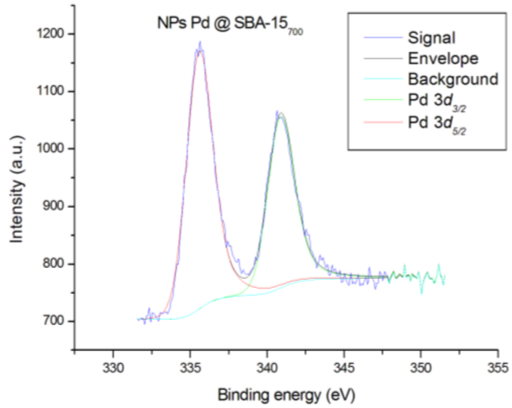


Figure S8 – XPS spectrum and deconvolution of Pd 3d core levels of Pd colloid impregnated on a SBA-15_{700} support.

Catalytic study

NMR study

The cross-coupling product (4-acetylbiphenyl) was isolated and analyzed by ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06-8.02 (m, 2H), 7.72-7.67 (m, 2H), 7.66-7.62 (m, 2H), 7.61—7.45 (m, 2H), 7.44-7.40 (m, 1H), 2.64 (s, 3H), and ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.9, 146.0, 140.1, 136.0, 129.1, 129.0, 128.4, 127.4, 127.3, 26.8. These data are in full agreement with literature.[1–3]

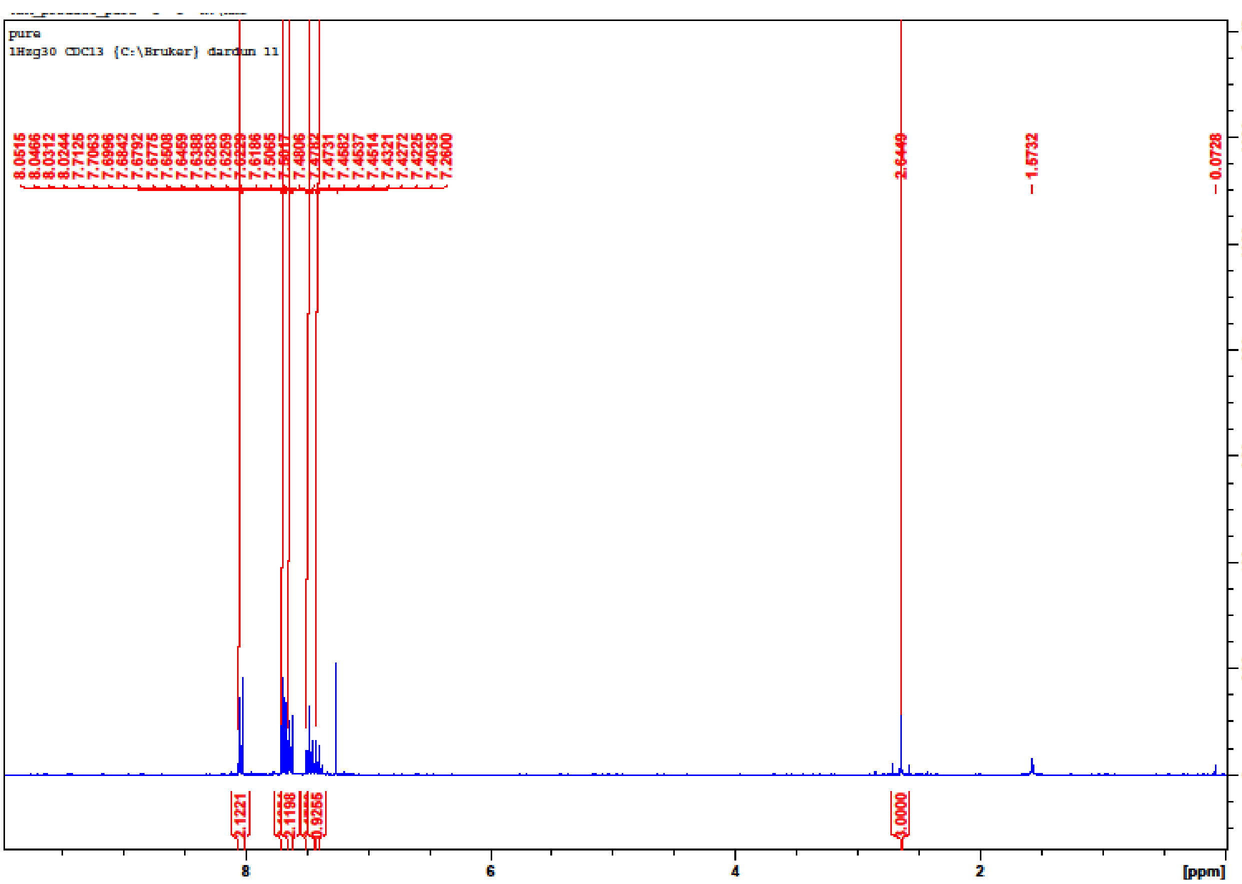


Figure S9 – ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the cross-coupling product (4-Acetylbiphenyl).

Chromatogram

A representative chromatogram is given in Figure S10, were the retention time and response factor are mentioned. All the reagents were bought and used to do a calibration curve prior to any kinetic measurements. *n*-Dodecane was used as internal standard.

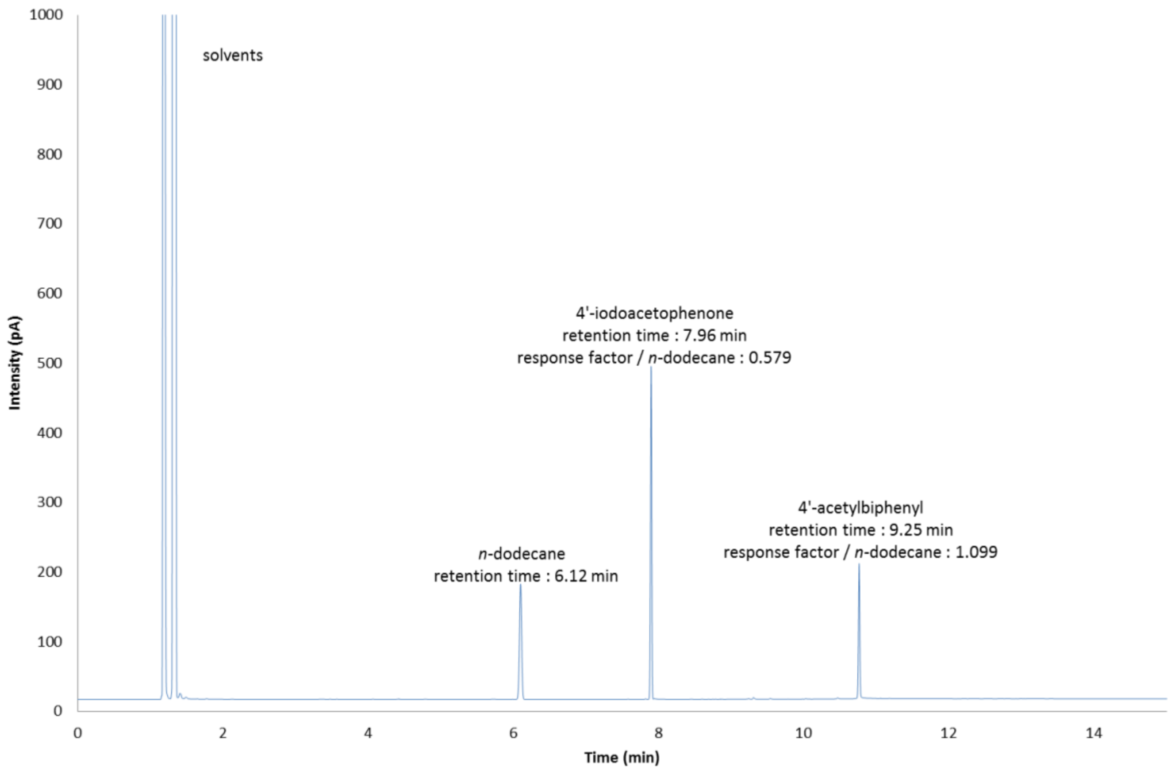


Figure S10 – Representative chromatogram obtained to measure the conversions and yields.

TON and TOF assessment

The productivity (TON) was measured using the formula: $\frac{amount\ of\ converted\ \ reactant\ (mmol)}{amount\ of\ total\ palladium\ (mmol)}$. For example, as 0.2 mol% is used and a complete conversion is achieved, the TON is 500.

The activity (TOF_{50}) was measured using the formula: $\frac{TON}{time\ (h)}$, and it was measured at ca. 50 % conversion (slope to the curve).

Catalytic tests

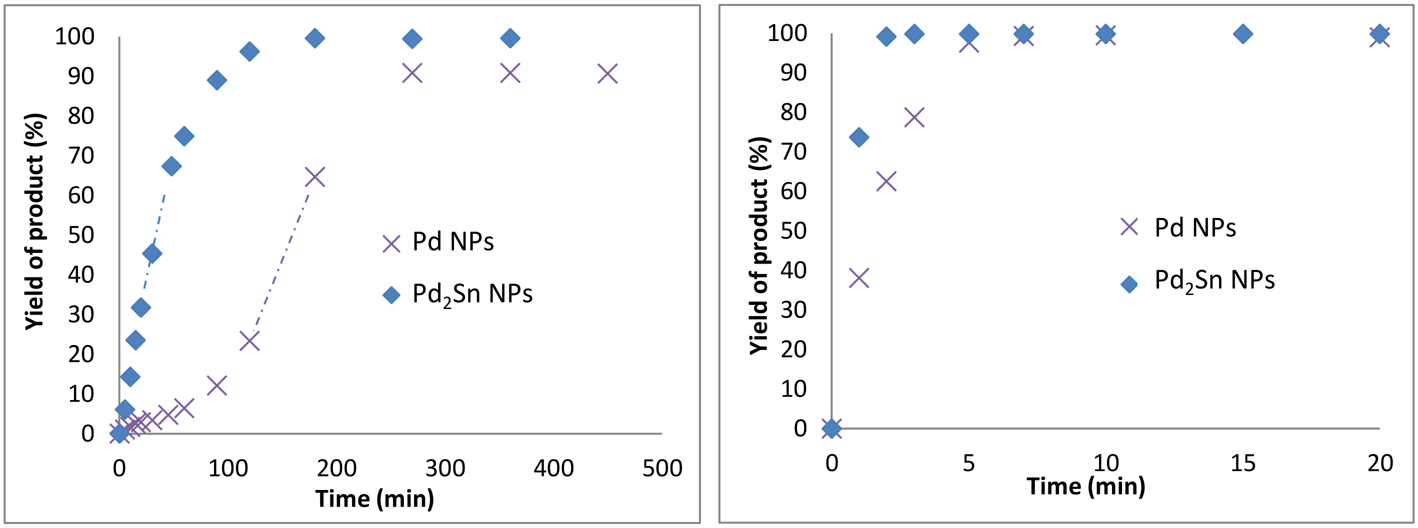


Figure S11 – Kinetic monitoring of the Suzuki-Miyaura cross-coupling reaction using Pd and Pd_2Sn colloidal catalysts at $2 \cdot 10^{-3}$ mol % (left) and 0.2 mol% (right) of total Pd. The slopes of the conversion/product yields vs. time at ca. 50 % conversion and shown here as blue and purple dash lines were used to calculate TOF_{50}.

The same procedure was used to compare the Pd NPs synthesized in THF or toluene. Despite the discrepancy at 1 minute due to a slightly different addition time of the catalyst, the activities of both catalysts are very similar measured between 1 and 3 minutes.

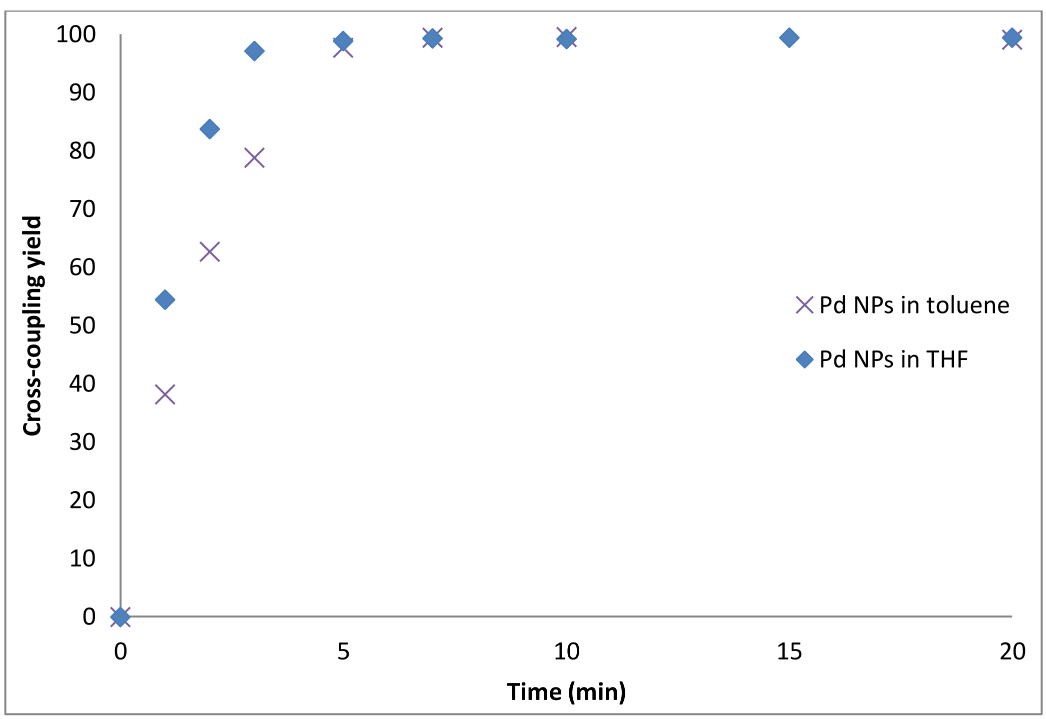


Figure S12 – Kinetic monitoring of the Suzuki-Miyaura cross-coupling reaction using Pd NPs in toluene or THF at 0.2 mol% of total Pd.

References

1 C. Nájera, J. Gil-Moltó, S. Karlström and L. R. Falvello, *Org. Lett.*, 2003, **5**, 1451–1454.

2 J. H. Li and W. J. Liu, *Org. Lett.*, 2004, **6**, 2809–2811.

3 H. Firouzabadi, N. Iranpoor, M. Gholinejad and F. Kazemi, *RSC Adv.*, 2011, **1**, 1013–1019.