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Supporting Information

Selective Alkyne Semi-Hydrogenation by PdCu Nanoparticles Immobilized on Stereocomplexed Poly(lactic acid)

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1. Syntheses

1.1. Syntheses of *l*-and *d*-PLA^{BiPy}

In a double-necked round-bottom flask, equipped with a condenser *l* or *d*-lactide (2.48 g, 17.23 mmol), toluene (20 mL), $Sn(Oct)_2$ (25.0 mg, 0.062 mmol) and BiPyOH (0.20 g, 1.00 mmol) were heated at 110 °C for 12 h under a nitrogen atmosphere. Afterward, the reaction mixture was cooled to room temperature and the solvent completely removed by means of a vacuum. The crude product was dissolved in CH_2Cl_2 (20 mL) and upon addition of *n*-hexane (50 mL) an off-white solid powder was obtained, which was separated from solution by filtration, washed several times with *n*-hexane (3×10 mL), and dried under vacuum at room temperature for 12 h. Yield: *l*-PLA^{BiPy} (2.34 g, 94%), *d*-PLA^{BiPy} (2.1 g, 84%). The molar mass (M_n) of both macroligands has been determined by ^{1}H NMR spectroscopy using the integral of the quartett at 5.23 ppm (*i.e*. repeating CH unit of PLA chain) and that at 4.37 ppm (*i.e*. CH group of the terminal lactic acid unit): *l*-PLA^{BiPy}, 4140 g/mol; *d*-PLA^{BiPy}, 3800 g/mol ^{1}H and $^{13}C\{^1H\}$ NMR data correspond to that reported to the same type of macroligands featured by a longer polymer chain.[S1]

1.2. Syntheses of Pd(OAc)$_2$(*l*/*d*-PLA^{BiPy}) and Cu(OAc)$_2$(*l*/*d*-PLA^{BiPy})

Pd(OAc)$_2$(*l*/*d*-PLA^{BiPy}) was synthesized following a synthesis protocol published by some of us.[S1] $Pd(OAc)_2$ (0.64mmol) was added to a solution of *l* or *d*-PLA^{BiPy} (0.64 mmol) in CH_2Cl_2 (10 mL) and the resulting solution was stirred under a nitrogen atmosphere at room temperature for 6 h. Afterward the solvent was removed completely under vacuum and the slightly yellow solid was washed with diethyl ether (2 × 5 mL) and dried under vacuum.

Yield: $Pd(AcO)_2$(*l*-PLA^{BiPy}), 900 mg (82.0%); $Pd(AcO)_2$(*d*-PLA^{BiPy}), 900 mg (73.2%). ^1H and $^{13}C\{^1H\}$ NMR data corresponded to that reported in the literature.[S1] XPS: Pd*3d*$_{5/2}$, B.E. = 337.2 eV and N*1*s, B.E. = 399.0 eV.

$Cu(OAc)_2$(*l*/*d*-PLA^{BiPy}) was synthesized by a modified synthesis protocol due to the low solubility of $Cu(OAc)_2$ in dichloromethane. $Cu(OAc)_2$ (0.76 mmol) and *l*/*d*-PLA^{BiPy} (0.64 mmol) were successively mixed together, milled in a porcelain mortar and then suspended in dichloromethane (10 mL), followed by stirring the suspension for 6 h at room temperature. The obtained almost clear green solution was filtered to remove excess $Cu(OAc)_2$ and upon addition of *n*-hexane (50 mL), the product precipitated as a green solid, which was separated by filtration, washed several times with *n*-hexane and dried under vacuum at room temperature for 12 h.

Yield: $Cu(AcO)_2$(*l*-PLA^{BiPy}), 910.0 mg (85%); $Cu(AcO)_2$(*d*-PLA^{BiPy}), 910 mg (76%). XPS: Cu*2p*$_{3/2}$, B.E. = 931.7 and 934.0 eV and N*1*s, B.E. = 399.0 eV.

1.3. Syntheses of $Pd(OAc)_2/Cu(OAc)_2$(*sc*-PLA^{BiPy}), $Pd(OAc)_2$(*sc*-PLA^{BiPy}) and $Cu(OAc)_2$(*sc*-PLA^{BiPy})

Equal amounts (200 mg) of $Cu(AcO)_2$(*l*-PLA^{BiPy}) and $Pd(AcO)_2$(*d*-PLA^{BiPy}), $Pd(AcO)_2$(*l*-PLA^{BiPy}) and $Pd(OAc)_2$(*d*-PLA^{BiPy}) as well as $Cu(OAc)_2$(*l*-PLA^{BiPy}) and $Cu(OAc)_2$(*d*-PLA^{BiPy}) were dissolved in dichloromethane (5 mL), mixed together and stirred at room temperature for half an hour before evaporating the solvent. Off-white solids of the stereocomplexed (*sc*) macrocomplexes $Pd(OAc)_2/Cu(OAc)_2$(sc-PLA^{BiPy}), $Pd(OAc)_2$(*sc*-PLA^{BiPy}) and $Cu(OAc)_2$(*sc*-PLA^{BiPy}) have been obtained in a yield range from 90 to 95%.

ICP-OES: $Pd(OAc)_2/Cu(OAc)_2$(*sc*-PLA^{BiPy}): Pd (1.35 wt%), Cu (0.85 wt%); $Pd(OAc)_2$(*sc*-PLA^{BiPy}): Pd (2.61 wt%); $Cu(OAc)_2$(*sc*-PLA^{BiPy}), Cu (1.71 wt%).

2. Figures

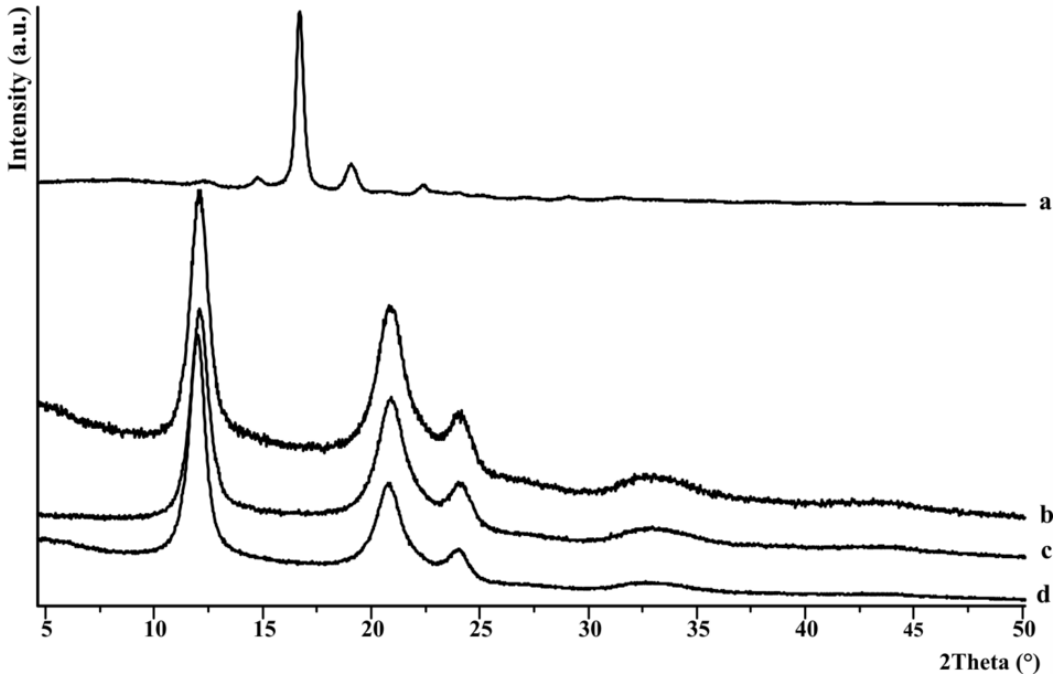


Figure S1. PXRD spectra for (*l*/*d*-PLA^{BiPy}) (a), $Pd(OAc)_2$(*sc*-PLA^{BiPy}) (b), $Pd(OAc)_2/Cu(OAc)_2$(*sc*-PLA^{BiPy}) (c) and $Cu(OAc)_2$(*sc*-PLA^{BiPy}) (d).

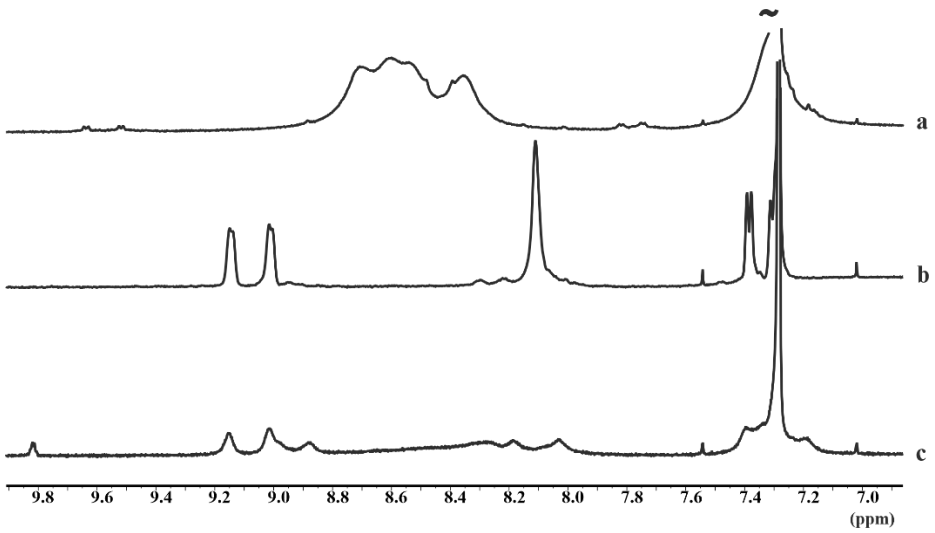


Figure S2. ^{1}H NMR spectra acquired in $CDCl_3$ at room temperature for *sc*-PLA^{BIPy} (a), Pd(OAc)$_2$(*sc*-PLA^{BiPy}) (b) and Pd(OAc)$_2$/Cu(OAc)$_2$(*sc*-PLA^{BiPy}) (c).

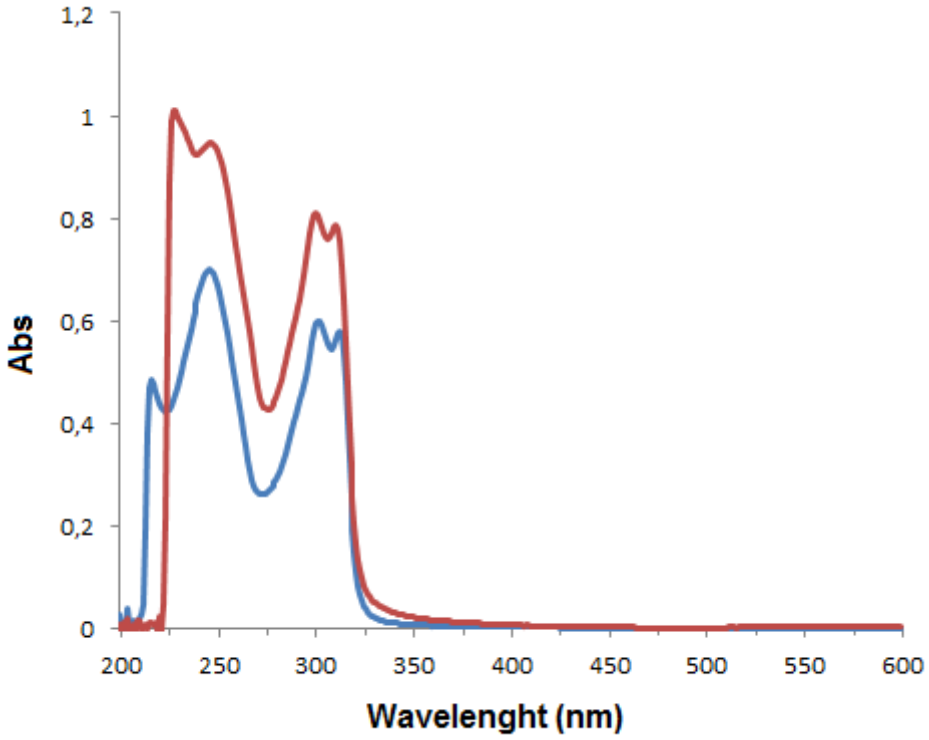


Figure S3. UV-vis spectra acquired in CH_2Cl_2 for Cu(OAc)$_2$(2,2'-bipyridine) (red trace) and Cu(OAc)$_2$(*l*-PLA^{BiPy}) (blue trace).

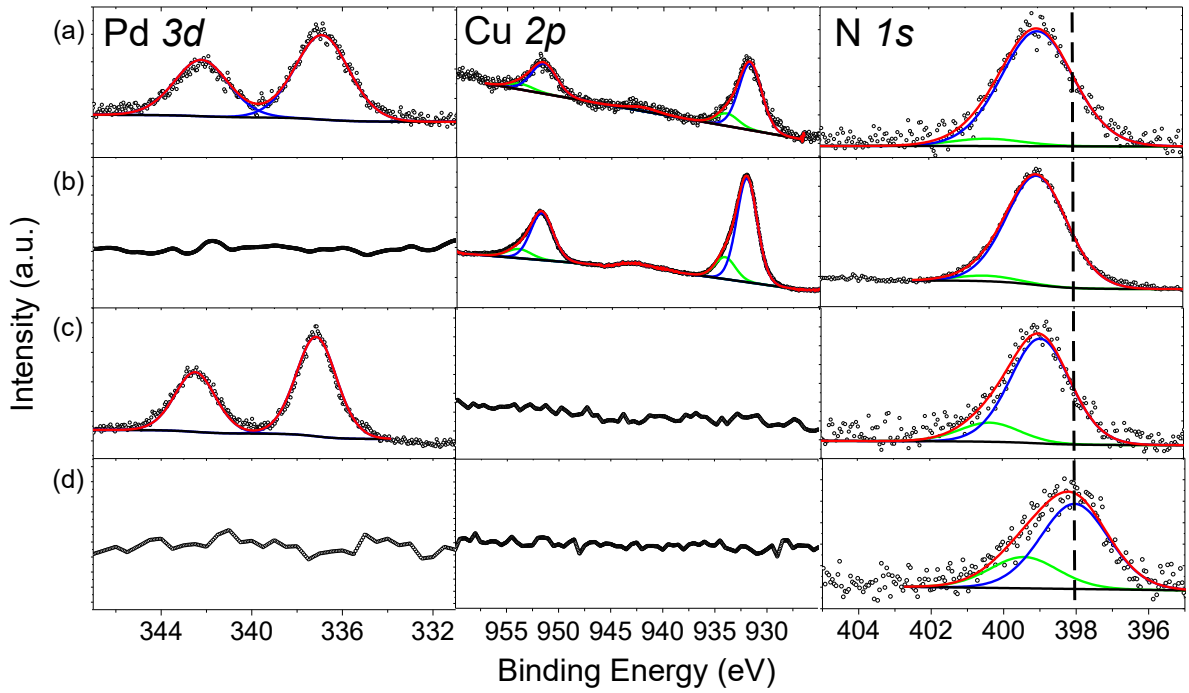


Figure S4. XPS spectra acquired in the Pd*3d*, Cu*2p* and N*1s* regions for $Pd(OAc)_2/Cu(OAc)_2$(*sc*-PLA^{BiPy}) (a), $Cu(OAc)_2$(*l*-PLA^{BiPy}) (b), $Pd(OAc)_2$(*l*-PLA^{BiPy}) (c) and *l*-PLA^{BiPy} (d).

Table S1. Relevant XPS data for *l*-PLA^{BiPy}, $Pd(OAc)_2/Cu(OAc)_2$(*sc*-PLA^{BiPy}), $Pd(OAc)_2$(*l*-PLA^{BiPy}), $Cu(OAc)_2$(*l*-PLA^{BiPy}), **[PdCu]**, **[Pd]** and **[Cu]**.

Compound	Pd$3d_{5/2}$ B.E. (eV) [Pd(II) (%)]	Cu$2p_{3/2}$ B.E. (eV) [Cu(II) (%)]	N *1s* B.E. (eV)	Pd/Cu atomic ratio	(Pd+Cu)/N atomic ratio
l-PLA^{BiPy}			398.0	-	-
$Pd(OAc)_2/Cu(OAc)_2$(*sc*-PLA^{BiPy})	336.8 [100]	931.7, 933.8 [16]	399.0	0.9	0.3
$Pd(OAc)_2$(*l*-PLA^{BiPy})	337.2 [100]	-	399.0	-	0.5
$Cu(OAc)_2$(*l*-PLA^{BiPy})	-	931.7, 934.0 [17.5]	399.0	-	0.6
[PdCu]-as synthesized	337.0/334.3 [58]	931.1, 933.9 [23]	398.7	0.1	0.5
[Pd]	337.0/334.4 [74]	-	398.8	-	0.6
[Cu]	-	931.4, 933.8 [26]	398.7	-	0.6
[PdCu]-recovered	336.8/334.2 [47]	931.5, 933.9 [32.5]	398.7	0.2	0.5

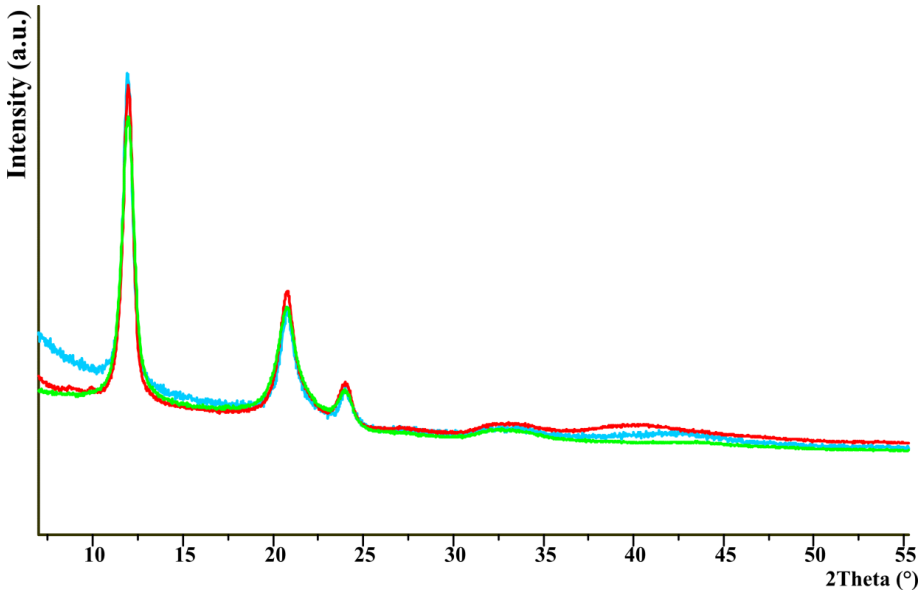


Figure S5. PXRD spectra for [**PdCu**] (blue trace), [**Pd**] (red trace) and [**Cu**] (green trace).

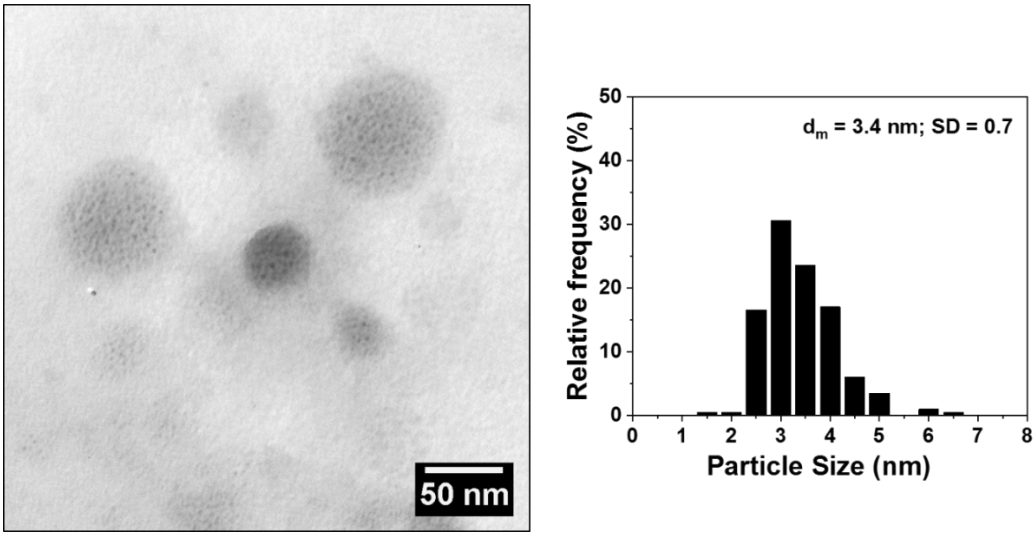


Figure S6. TEM micrograph and histogram of the particle size distribution in **[Cu]**.

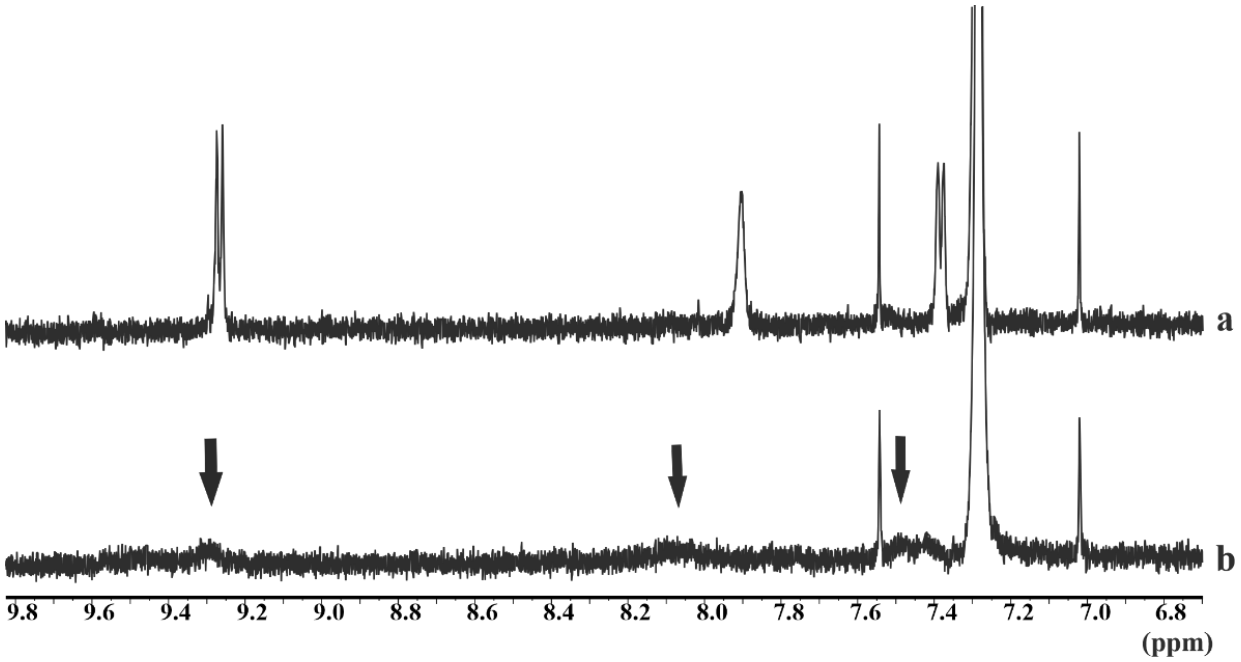


Figure S7. ^{1}H NMR spectra acquired in $CDCl_3$ for **[Pd]** (a) and **[PdCu]** (b).

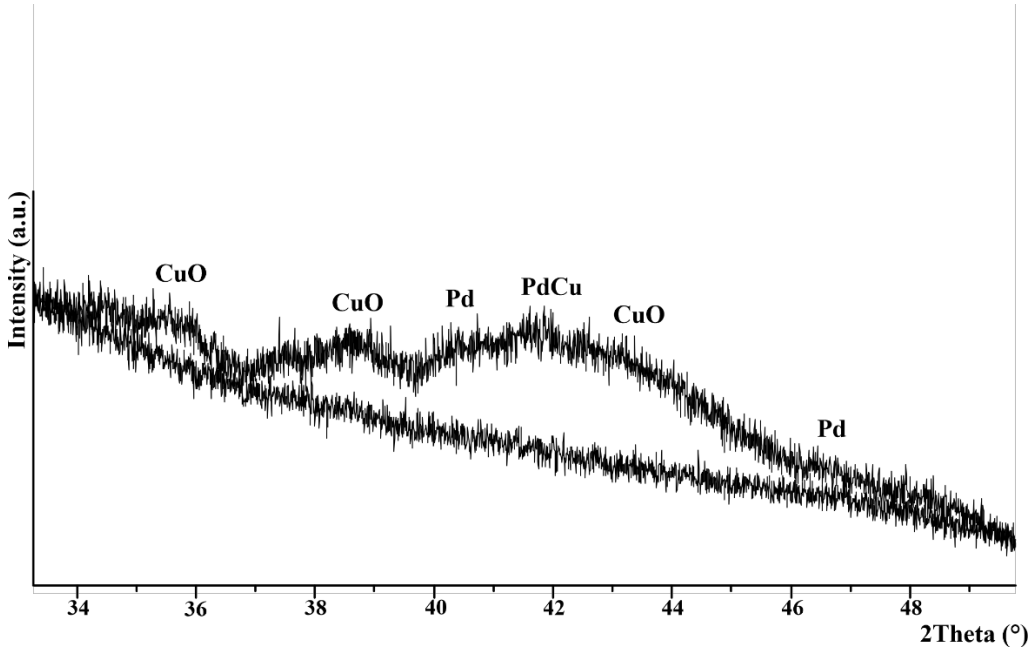
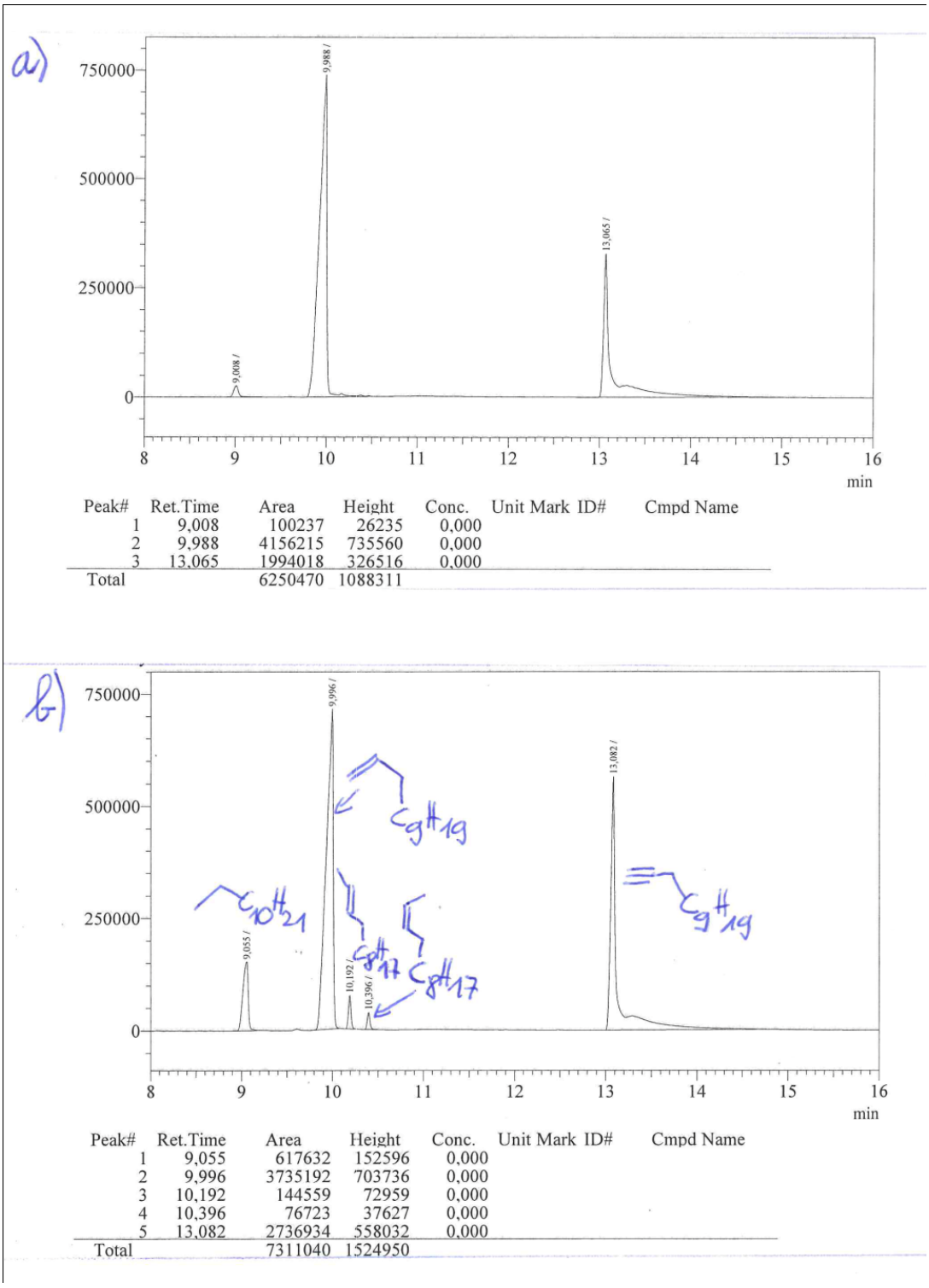


Figure S8. PXRD spectra acquired in the 2Θ range 33-50° for a 1:1 mixture of $Pd(OAc)_2$(*d*-PLA^{BiPy}) and $Cu(OAc)_2$(*d*-PLA^{BiPy}) (lower trace) and after treatment with hydrogen in CH_2Cl_2 (upper trace).



Peak#	Ret.Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	9,008	100237	26235	0,000			
2	9,988	4156215	735560	0,000			
3	13,065	1994018	326516	0,000			
Total		6250470	1088311				

Peak#	Ret.Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	9,055	617632	152596	0,000			
2	9,996	3735192	703736	0,000			
3	10,192	144559	72959	0,000			
4	10,396	76723	37627	0,000			
5	13,082	2736934	558032	0,000			
Total		7311040	1524950				

Figure S9. Gas chromatograms acquired for **[PdCu]** (a) and **[Pd]** (b) catalyzed 1-dodecyne hydrogenation reactions conducted in EtOH.

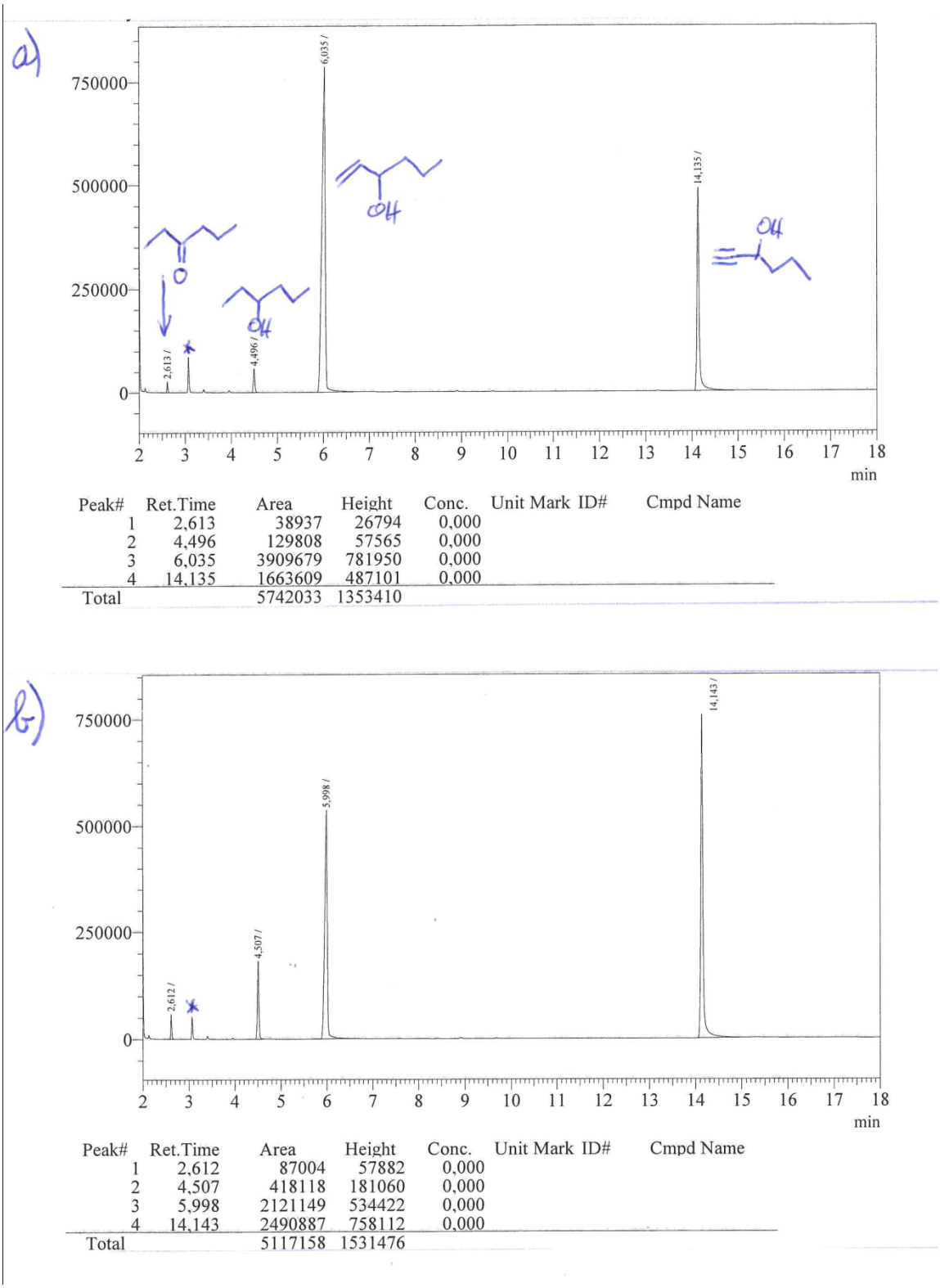
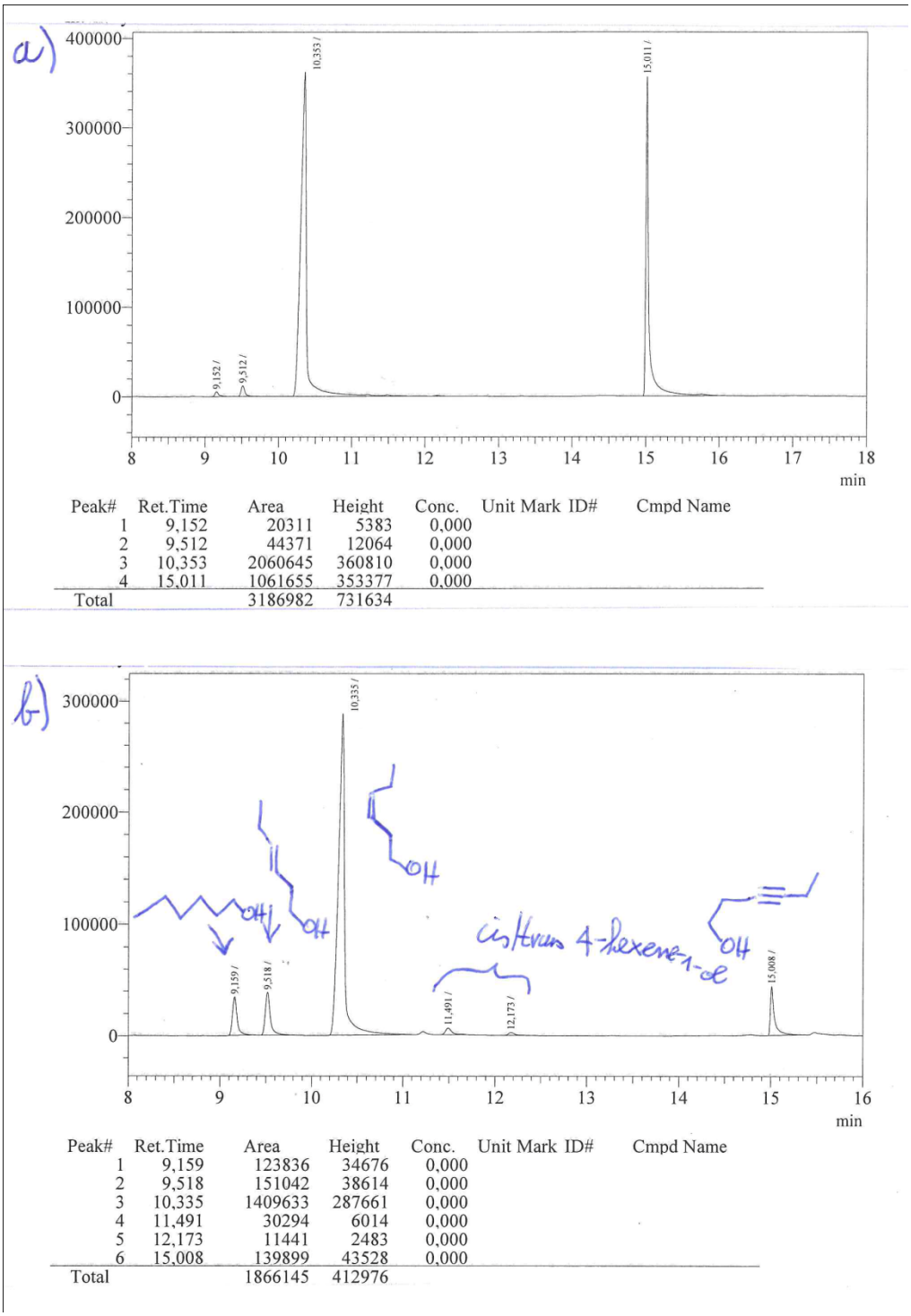


Figure S10. Gas chromatograms acquired for **[PdCu]** (a) and **[Pd]** (b)-catalyzed 1-hexyn-3-ol hydrogenation reactions conducted in EtOH. Asterisk denotes an impurity present in purchased 1-hexyn-3-ol.



Peak#	Ret.Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	9,152	20311	5383	0,000			
2	9,512	44371	12064	0,000			
3	10,353	2060645	360810	0,000			
4	15,011	1061655	353377	0,000			
Total		3186982	731634				

Peak#	Ret.Time	Area	Height	Conc.	Unit Mark	ID#	Cmpd Name
1	9,159	123836	34676	0,000			
2	9,518	151042	38614	0,000			
3	10,335	1409633	287661	0,000			
4	11,491	30294	6014	0,000			
5	12,173	11441	2483	0,000			
6	15,008	139899	43528	0,000			
Total		1866145	412976				

Figure S11. Gas chromatograms acquired for **[PdCu]** (a)- and **[Pd]** (b)-catalyzed 3-hexyn-1-diol hydrogenation reactions conducted in EtOH.

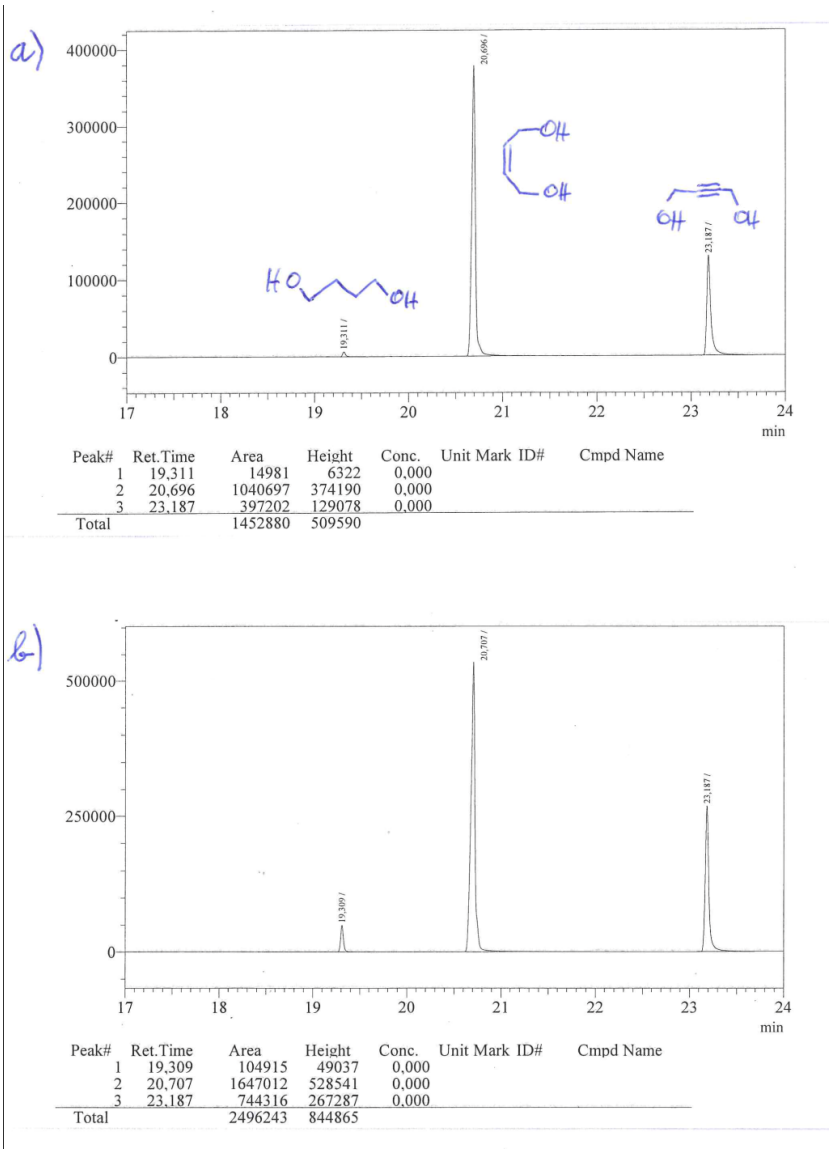


Figure S12. Gas chromatograms acquired for **[PdCu]** (a)-and **[Pd]** (b)-catalyzed 2-butyn-1,4-diol hydrogenation reactions conducted in EtOH.

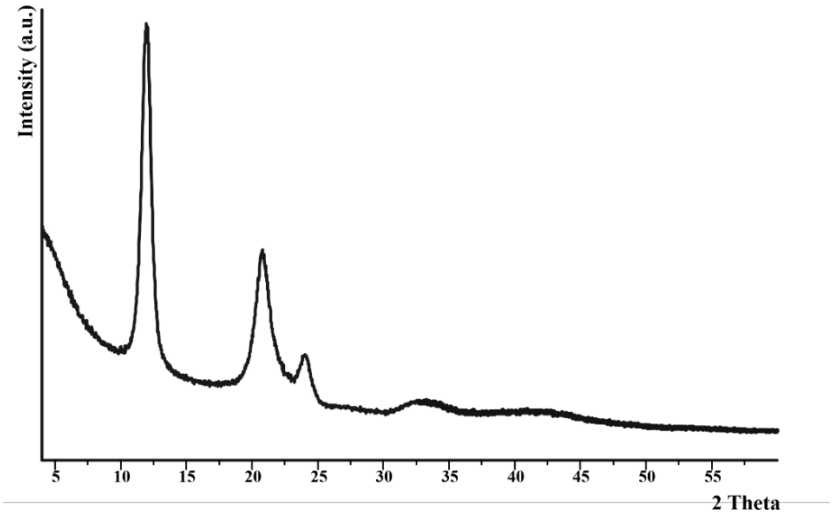
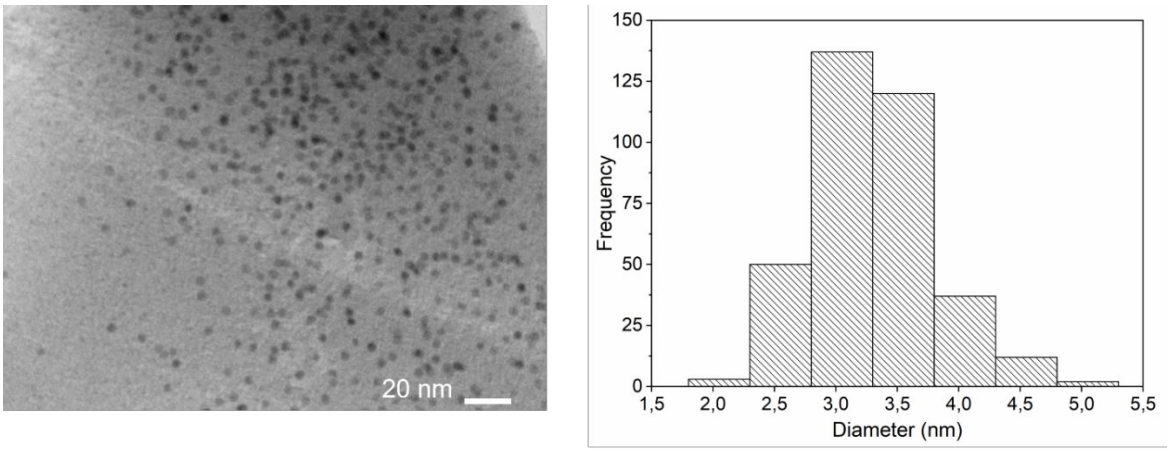


Figure S13. PXRD spectrum acquired for recovered **[PdCu]** (after the fourth catalytic cycle).



3. References

[S1] a) W. Oberhauser, C. Evangelisti, R. P. Jumde, G. Petrucci, M. Bartoli, M. Frediani, M. Mannini, L. Capozzoli, E. Passaglia, L. Rosi, *J. Catal.* **2015**, *330*, 187-196; b) M. Frediani, W. Oberhauser, L. Rosi, M. Bartoli, E. Passaglia, L. Capozzoli, *Rend. Fis. Acc. Lincei* **2017**, *28*, S51-S58; c) G. Petrucci, W. Oberhauser, M. Bartoli, G. Giachi, M. Frediani, E. Passaglia, L. Capozzoli, L. Rosi, *Appl. Catal. A: Gen*. **2014**, *469*, 132-138.