Supporting Information

Palladium-heterogenized Porous Polyimides Materials as Effective and Recycable Catalysts for reactions in Pure Water

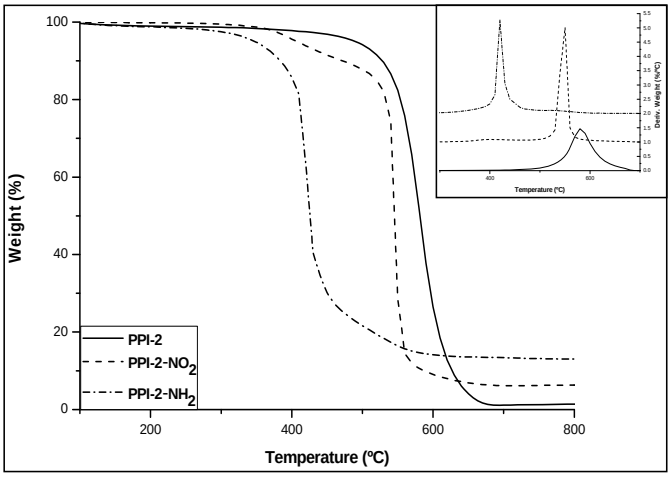
E. Rangel Rangel,[a] E. M. Maya, [a] F. Sánchez,[b] J.G. de la Campa,[a] and M. Iglesias[c]

1.- CHARACTERIZATION OF PPI-n-MATERIALS

Characterization techniques

Elemental analysis (%C, %N and %H) were determined in a LECO CHNS-932 analyzer. *ATR- FTIR spectra* were recorded on a PerkinElmer Spectrum One spectrometer and are reported in terms of frequency of absorption (cm^{-1}). *^{13}C solid-state NMR* measurement was recorded with a Bruker AV400 WB spectrometer (Larmor frequency of 100 MHz, using 4 mm MAS probes spinning at 10 kHz rate). *Thermogravimetric analyses (TGA)* were conducted in a TA-Q500 analyzer. The samples were heated under an air stream from 40 to 850ºC with a heating rate of 10ºC/min. *WAXS (wide-angle X-ray scattering)* was carried out with a Bruker D8 Advance diffractometer. Data were collected stepwise over the $1º \leq 2\theta \leq 65º$ angular region, with steps of 0.5 s/step accumulation time and Vantec detector and CuKα (λ = 1.542 Å) radiation. *Specific surface area measurement and porosity analysis* were performed using N_2 adsorption isotherms (Micromeritic, ASAP 2020 MICROPORE dry Analyzer) using the BET technique for surface area calculation and the BJH method for average pore size and pore volume calculations. Prior to measurement, the samples were degassed for 12 h at 100 ºC. *Palladium contents were analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)* on a PerkinElmer OPTIMA 2100 DV. *Scanning electron microscopy (SEM) micrographs* were obtained with a Hitachi SU-8000 microscope operating at 0.5 kV. The samples were prepared directly by dispersing the powder onto a double-sided adhesive surface. The reaction was monitored by gas chromatography on an HP5890 II GC-MS chromatograph, cross-linked methyl silicone column (SPB): 25 m x 0.2 mm x 0.33 mm.

Fig. S1a. Thermograms in air atmosphere of (a) **PPI-1**, **PPI-1-NO_2** and **PPI-1-NH_2**; (b) **PPI-2**, **PPI-2-NO_2** and **PPI-2-NH_2**



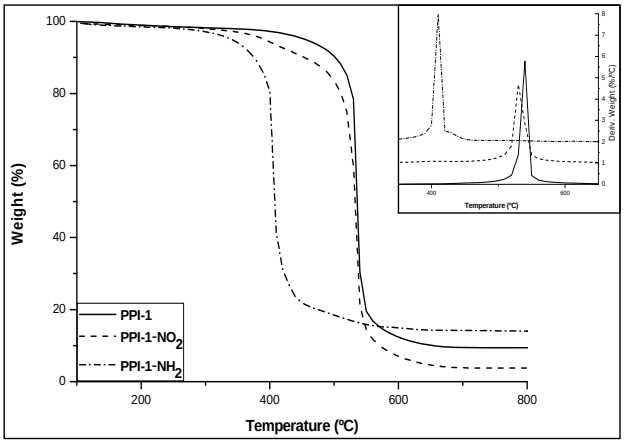
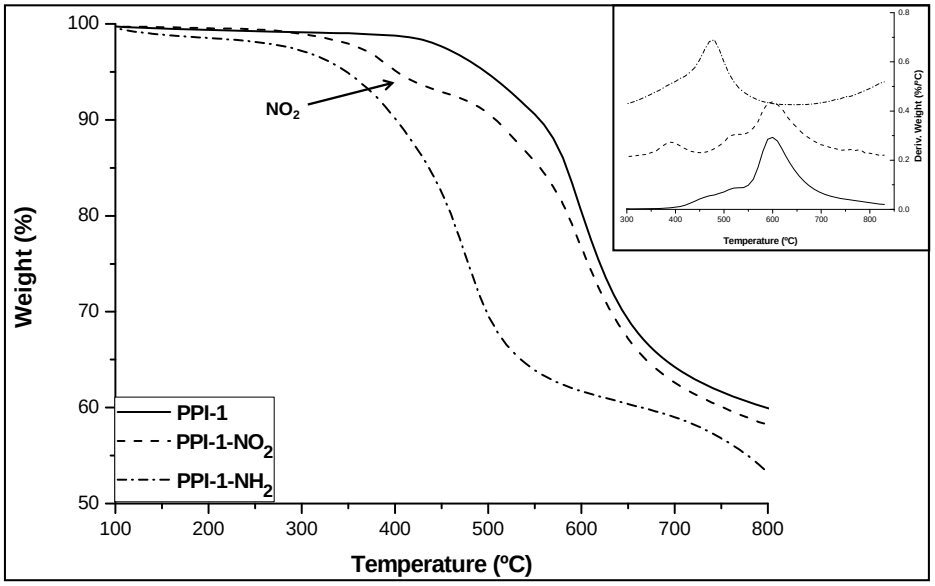


Fig. S1b. Thermograms in nitrogen atmosphere of (a) **PPI-1**, **PPI-1-NO_2** and **PPI-1-NH_2**; (b) **PPI-2**, **PPI-2-NO_2** and **PPI-2-NH_2**



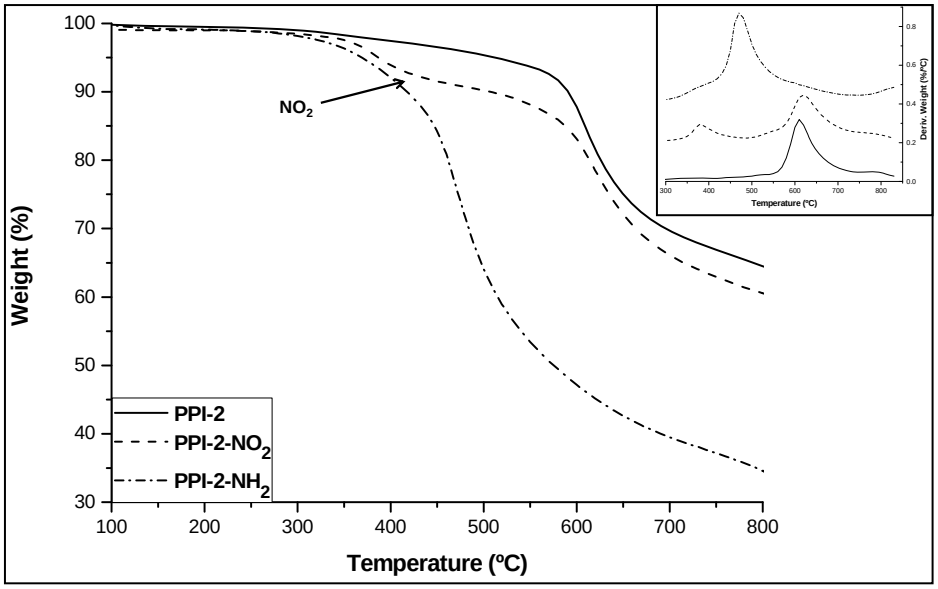


Fig. S2 Nitrogen sorption isotherm of **PPI-1, PPI-2, PPI-1-NH_2 and PPI-2-NH_2.**

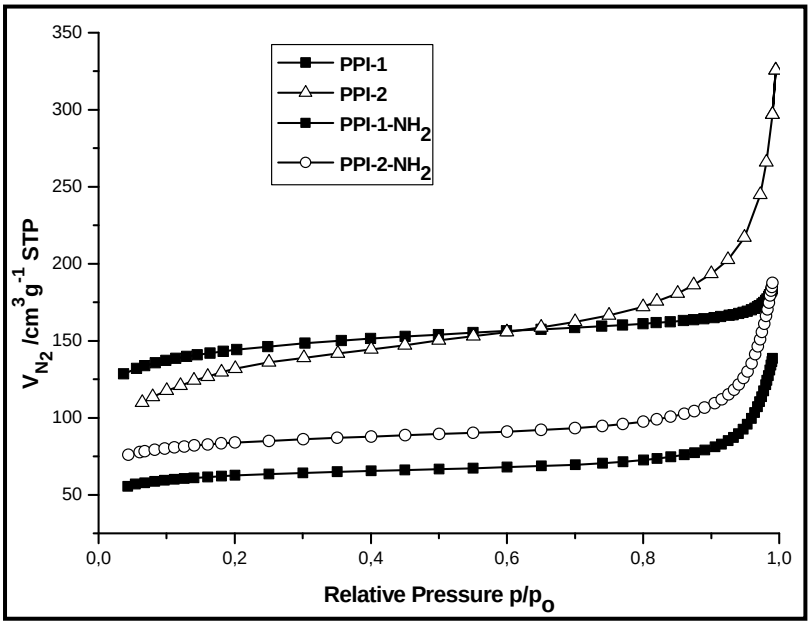


Fig. S3 Pore-size distribution of **PPI-1, PPI-2, PPI-1-NH_2 and PPI-2-NH_2.**

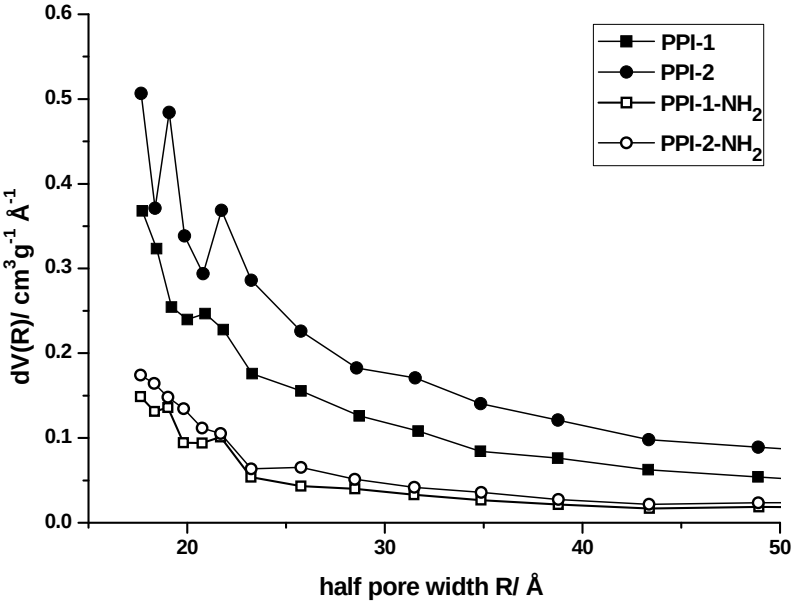


Fig. S4 Scanning electron micrographs (SEM) of **PPI-1, PPI-1-NO_2**, **PPI-2** and **PPI-2-NO2**

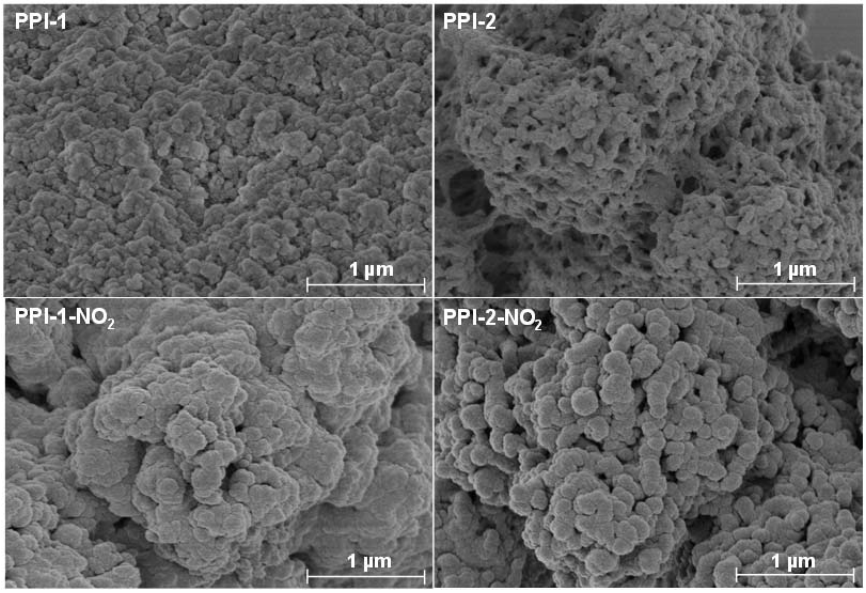
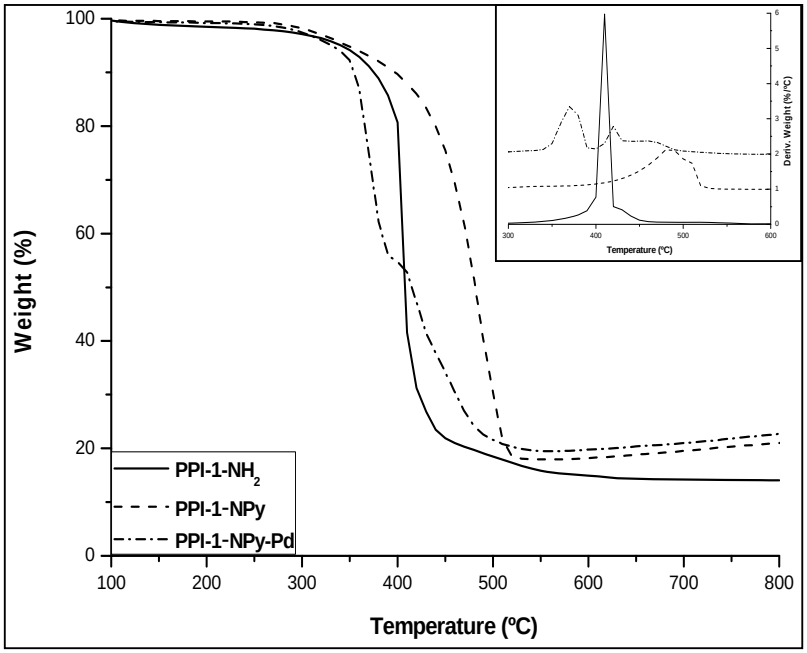


Fig. S5. TGA and DTG (Vertically shifted) of (a) PPI-1-NH_2, PPI-1-NPy and PPI-1-NPy-Pd (b) PPI-2-NH_2, PPI-2-NPy and PPI-2-NPy-Pd.



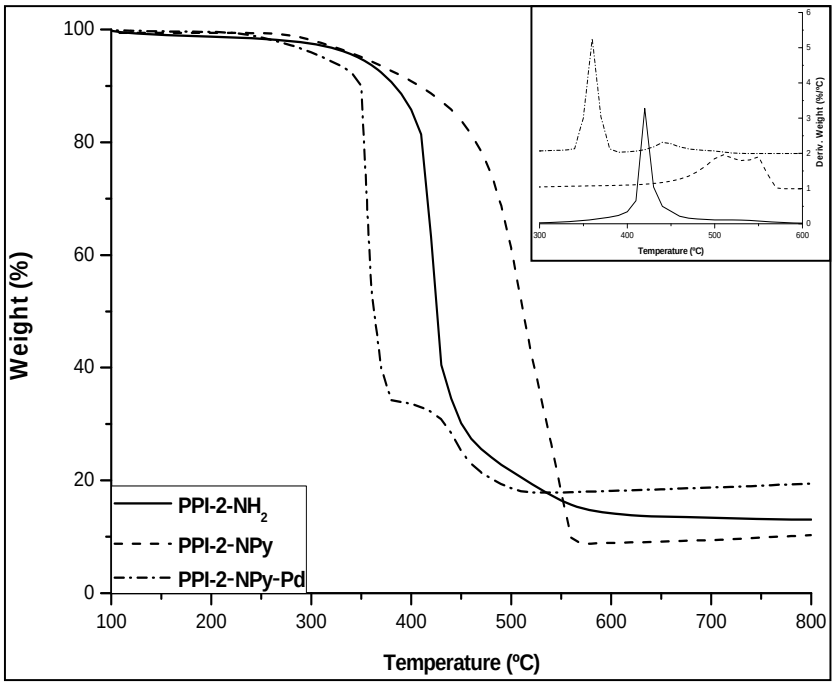


Fig. S6 ^{13}C-NMR solid spectra of **PPI-2-NH_2, PPI-2-NPy and PPI-2-NPy-Pd.**

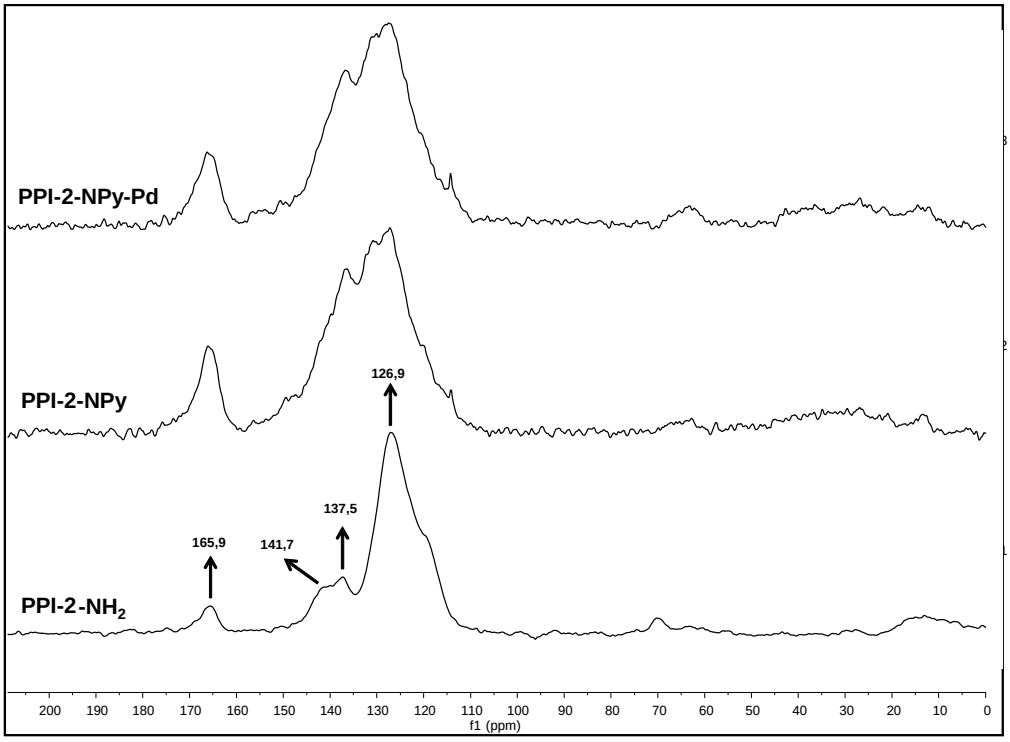


Table S1. Elemental analysis of starting, amino-functionalized porous polyimides

	% Calculated			% Experimental		
Polyimide	**C**	**H**	**N**	**C**	**H**	**N**
PPI-1-NH_2	71.15	2.77	9.22	55.49	3.66	6.03
PPI-1-NPy	72.17	2.83	9.91	58.80	3.67	6.66
PPI-1-NPy-Pd	59.69	2.34	8.19	55.77	3.29	6.25
PPI-2-NH_2	73.24	2.97	8.76	56.76	3.73	6.25
PPI-2-NPy	74.17	3.02	9.61	60.78	3.54	6.99
PPI-2-NPy-Pd	66.14	2.69	8.57	55.25	3.43	6.42

Fig. S7. [1]H-NMR spectra of **NPy** and **NPy-Pd**

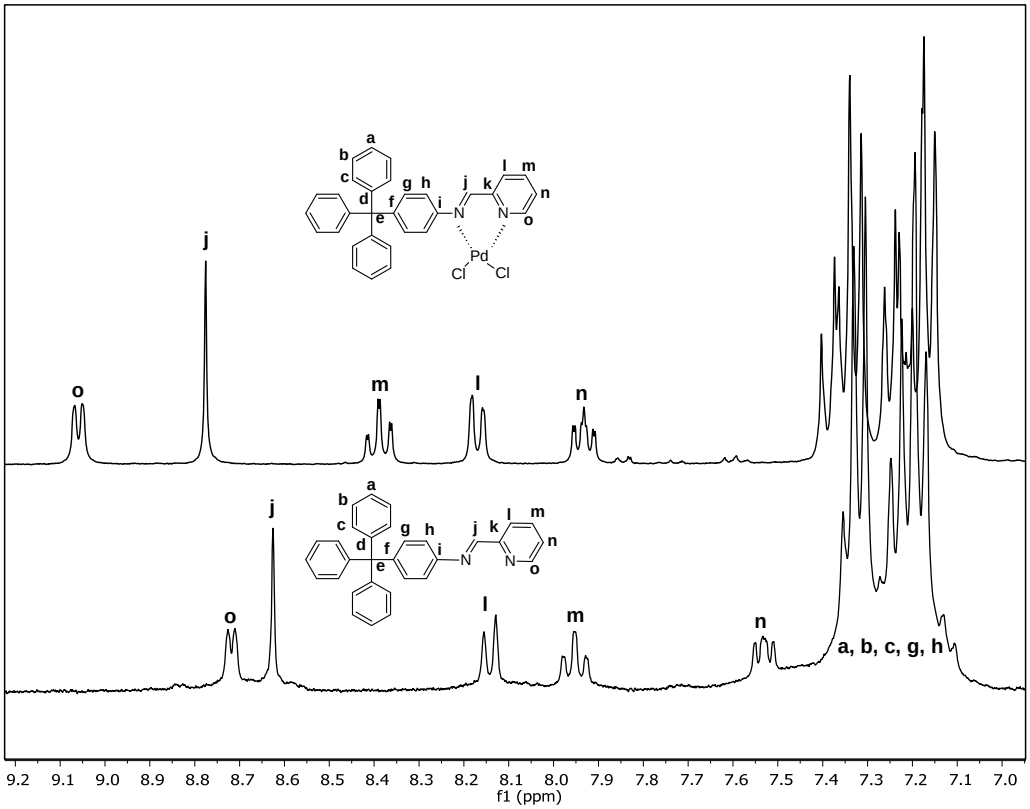


Fig. S8. [13]C-NMR spectra of **NPy** and **NPy-Pd**

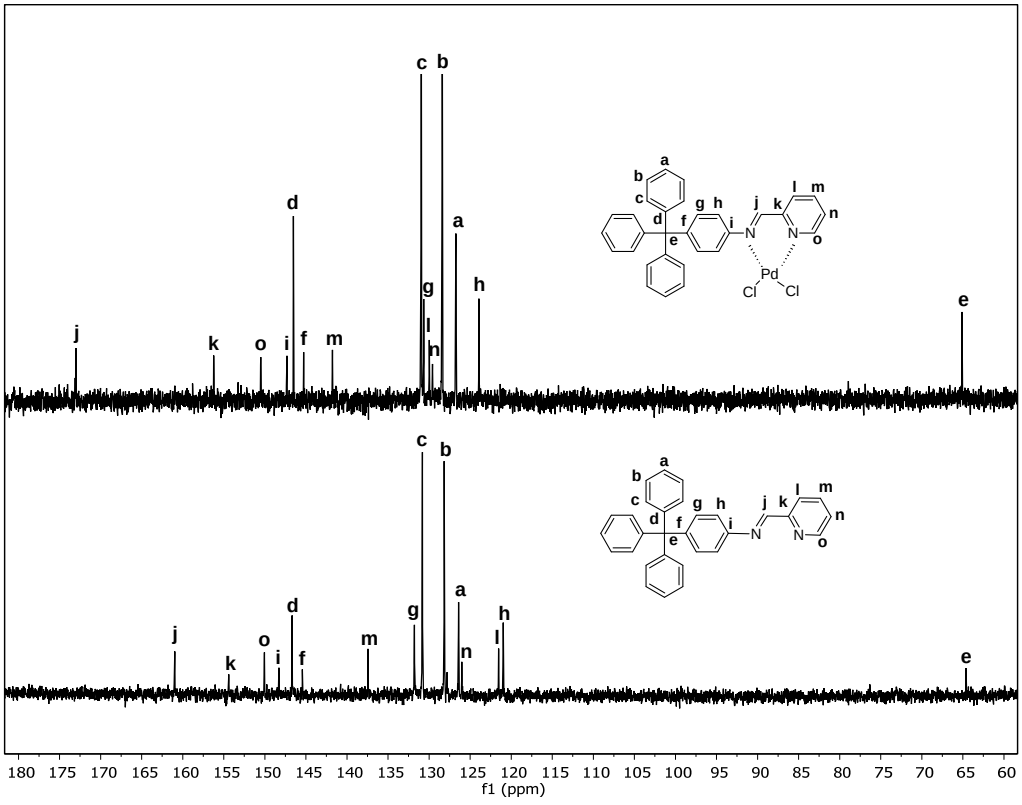
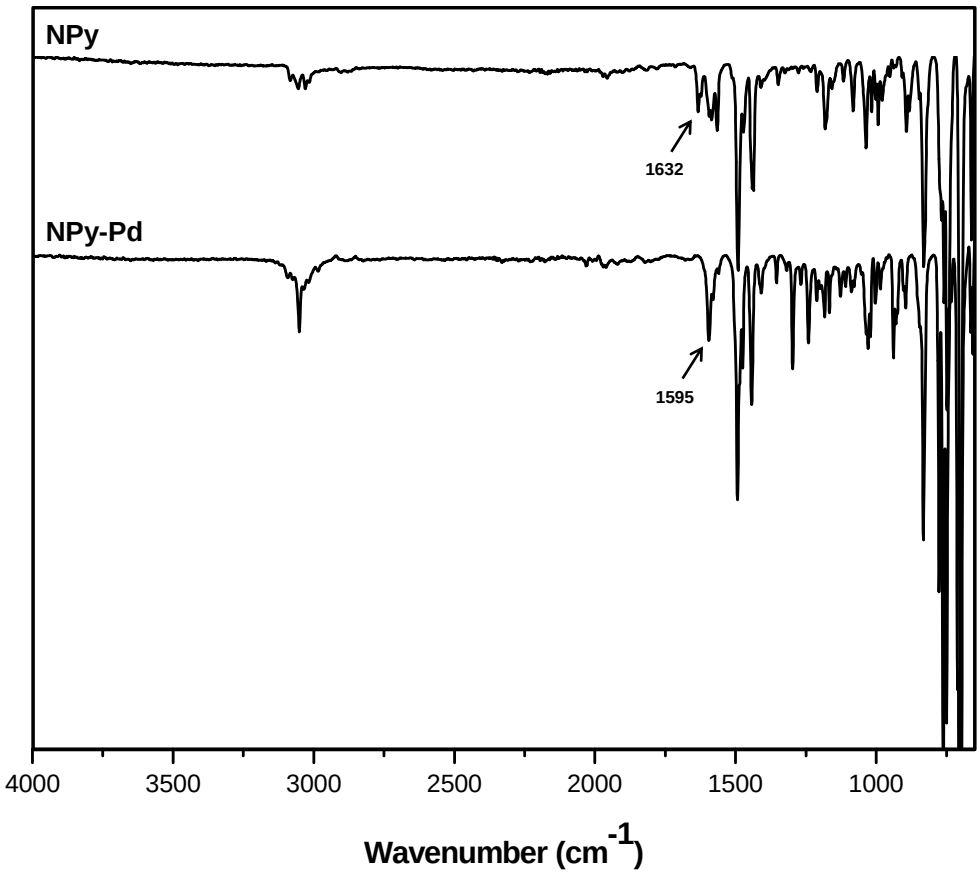


Fig. S9. FT-IR spectra of **NPy** and **NPy-Pd**



2.- CATALYTIC STUDIES

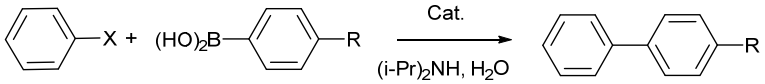
Optimization of reaction conditions

Table S2. Suzuki coupling reactions of iodobenzene with phenylboronic acid catalyzed by PPI-1-NPy-Pd.

	Cat. mol. (%)[b]	Solvent	Base	T (ºC)	t (h)	Yield (%)[c]	TOF (h^{-1})[d]
1	1.4	Xylene	K_2CO_3	130	48	14	-
2	1.4	H_2O	No base	90	48	2	-
3	1.4	H_2O	K_2CO_3	90	24	92	5.8
4	1.2	H_2O	NEt_3	100	1	86	72
5	1.2	H_2O	$(i\text{-}Pr)_2NH$	100	1	93	77
6	0.5	H_2O	$(i\text{-}Pr)_2NH$	100	1	73	134
7	0.3	H_2O	$(i\text{-}Pr)_2NH$	100	3	88	462
8	No catalyst	H_2O	$(i\text{-}Pr)_2NH$	100	24	-	-

[a]Reaction conditions: iodobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), solvent (1 ml). [b]Based on Pd; [c]Yield determined by GC and GCMS analysis; [d]mmol subs./mmol cat. h

Table S3. Suzuki coupling reactions of bromobenzene with various arylboronic acids catalyzed by PPI-1-NPy-Pd and NPy-Pd using water as solvent, DIPA as base at 100 ºC.



X	R	Catalysts	% mol Pd	T (h)	Conv. (%)
Br	**OMe**	PPI-1-NPy-Pd	0.5	1 2 3	27 75 93
Br	**COH**	PPI-1-NPy-Pd	0.4	0.5 1 1.5	14 43 85
Br	**CN**	PPI-1-NPy-Pd	0.8	3 4 5	2 48 93
Br	**OMe**	NPy-Pd	0.5	0.5 1 2 3	22 32 35 43
Br	**COH**	NPy-Pd	0.4	0.5 1 1.5 2	5 43 48 49
Br	**CN**	NPy-Pd	0.8	3 4 5	2.5 4 4

Fig. S10. Kinetic profiles for the PPI-1-NPy-Pd-catalyzed Suzuki reactions between bromobenzene and arylboronic acids (0.4-0.8 mol% Pd).

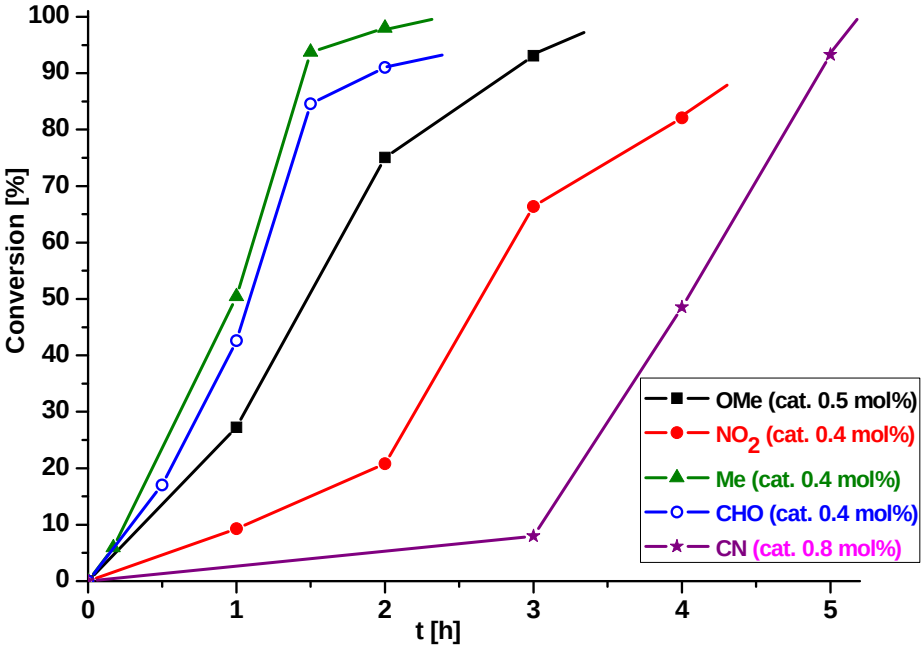
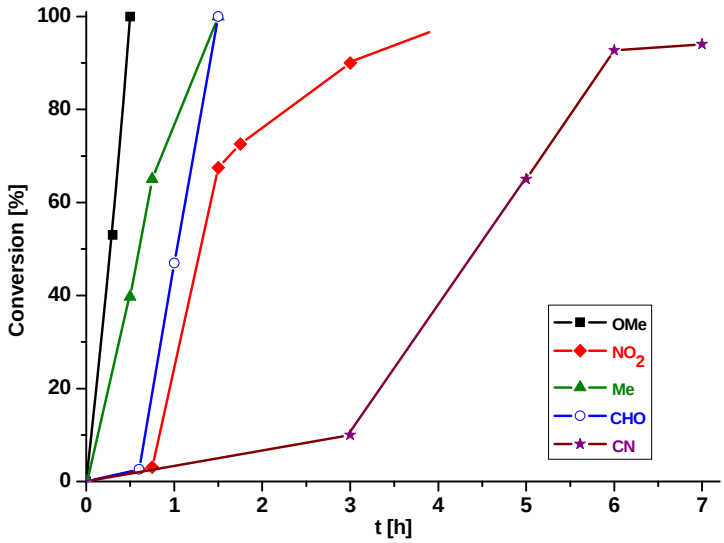


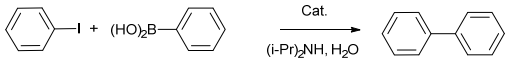
Fig. S11. Kinetic profile for the PPI-2-NPy-Pd-catalyzed Suzuki reactions between bromobenzene and arylboronic acids (0.5 mol% Pd).



Catalyst recyclability experiments:

For the recyclability experiment, after each catalytic experiment, the catalyst from the reaction pot was isolated by filtration, washed thoroughly and used for the next cycle of experiment under same reaction condition.

Table S4. Recyclability of PPI-1-NPy-Pd for Suzuki coupling reaction



Entry	Run	Conv. (%) (5 h)	TON (5 h)	TOF (h^{-1})
1	1	100	200	150
2	2	98	196	75
3	3	89	178	62
4	4	86	172	58
5	5	86	172	56
6	6	85	170	54
7	7	83	166	53

TON = mmol substrate/mmol cat. TOF= mmol subst/mmol cat. h

Fig. S12. Recycling experiments for Suzuki reaction between bromobenzene and 4-methoxyphenylboronic acid.

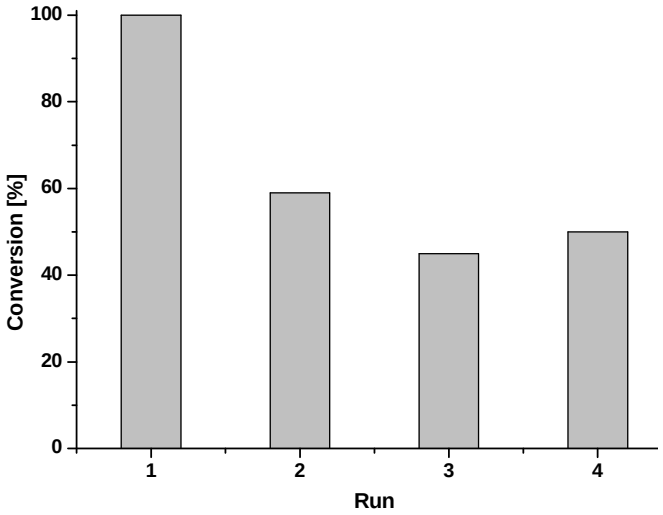


Table S5. Recyclability of PPI-2-NPy-Pd for Suzuki coupling reaction between bromobenzene and 4-methoxyphenylboronic acid.

Entry	Run	Conv. (%) (5 h)	TON	TOF (h^{-1})
1	1	100	200	200
2	2	62	118	26
3	3	42	64	9
4	4	48	86	15

TON = mmol substrate/mmol cat. TOF= mmol subst/mmol cat. h.

Fig. S13. FT-IR spectra of **PPI-n-NPy-Pd** catalysts before and after recycling.

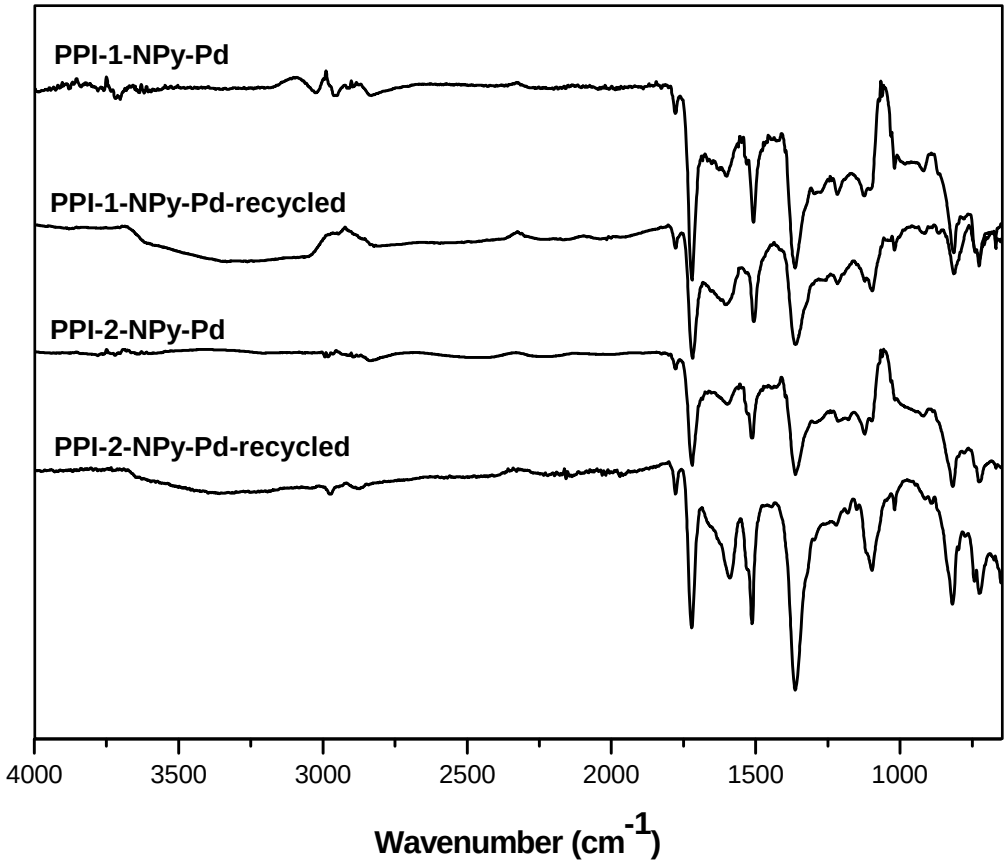


Fig. S14. WAXS difractograms of **PPI-n-NPy-Pd** catalysts before and after recycling.