Supplementary Materials: *P*-Stereogenic Phosphines for the Stabilisation of Metal Nanoparticles. A Surface State Study

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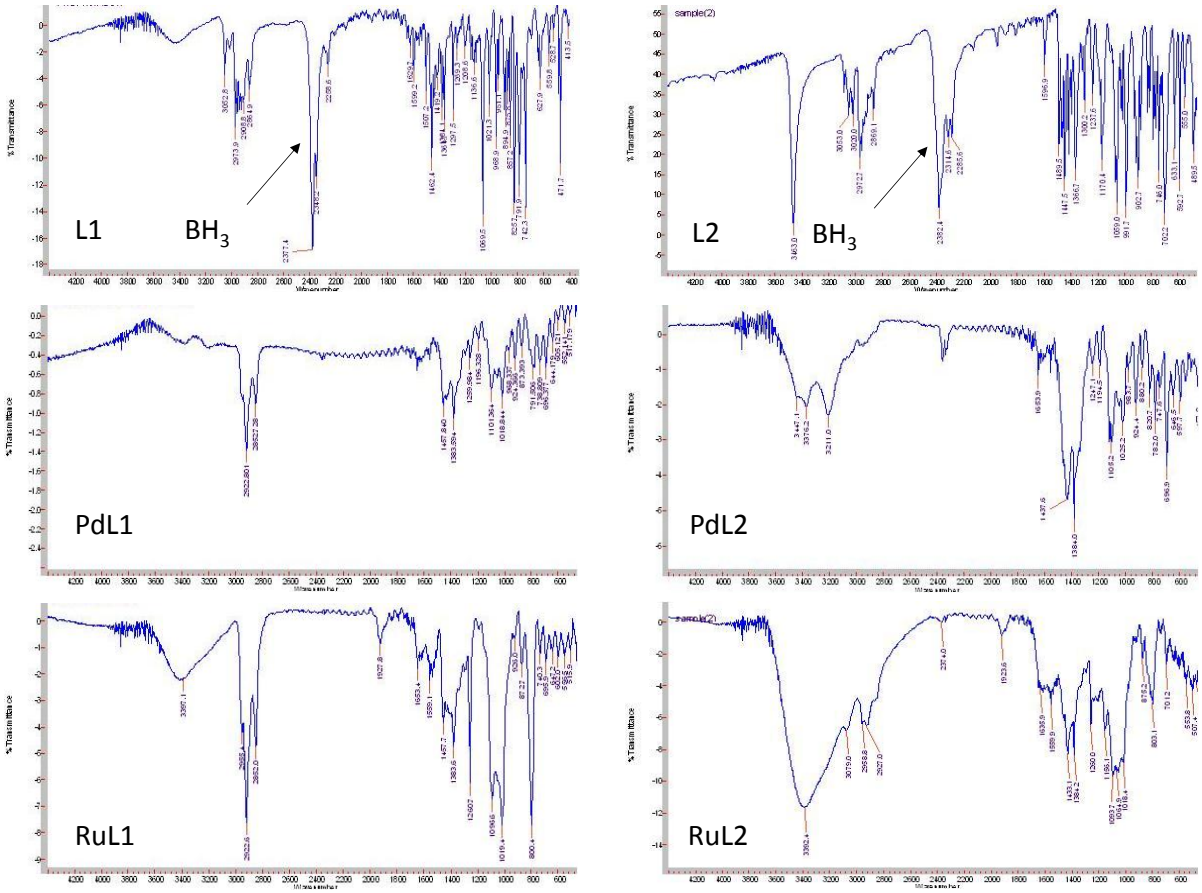


Figure S1. IR spectra (KBr pellets) of ligands **L1** and **L2** and the corresponding MNPs: **PdL1**, **PdL2**, **RuL1** and **RuL2**.

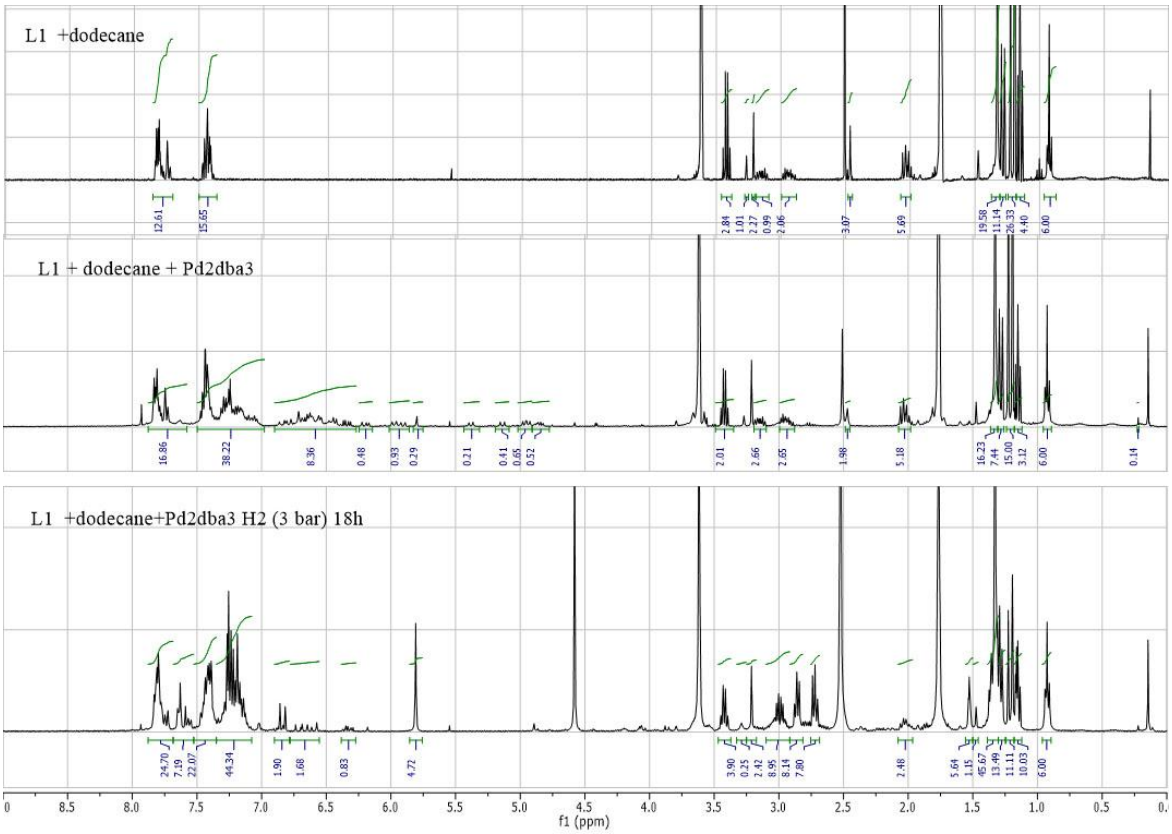


Figure S2. ^{1}H NMR (400 MHz, solvent, 298 K) spectra corresponding to the monitoring of the formation of **PdL1**.

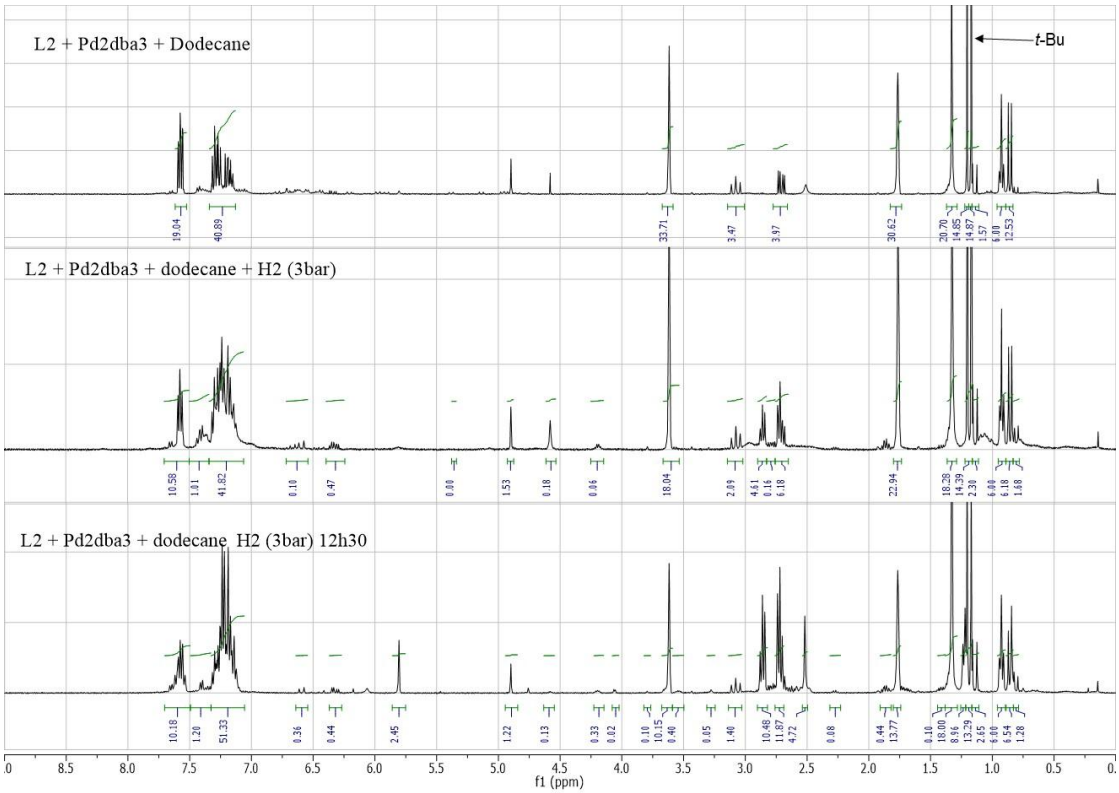


Figure S3. ^{1}H NMR (400 MHz, solvent, 298 K) spectra corresponding to the monitoring of the formation of **PdL2**.

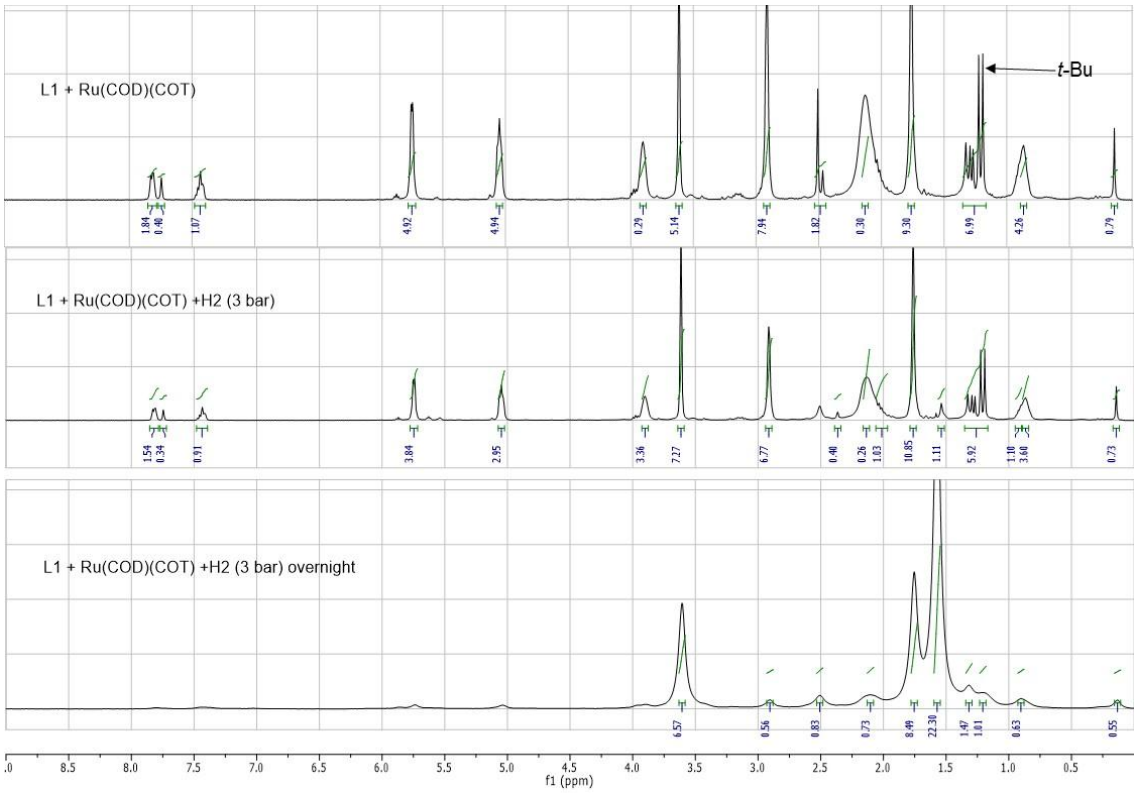


Figure S4. ^{1}H NMR (400 MHz, solvent, 298 K) spectra corresponding to the monitoring of the formation of **RuL1**.

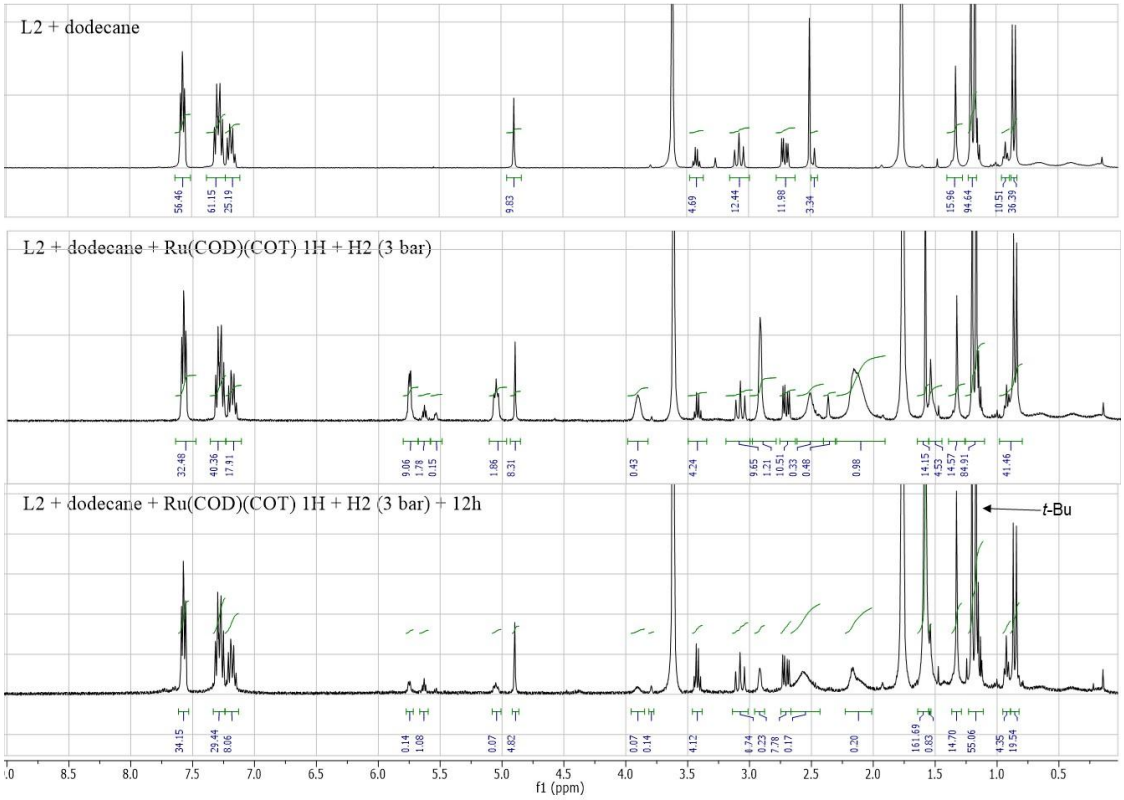


Figure S5. ^{1}H NMR (400 MHz, solvent, 298 K) spectra corresponding to the monitoring of the formation of **RuL2**.

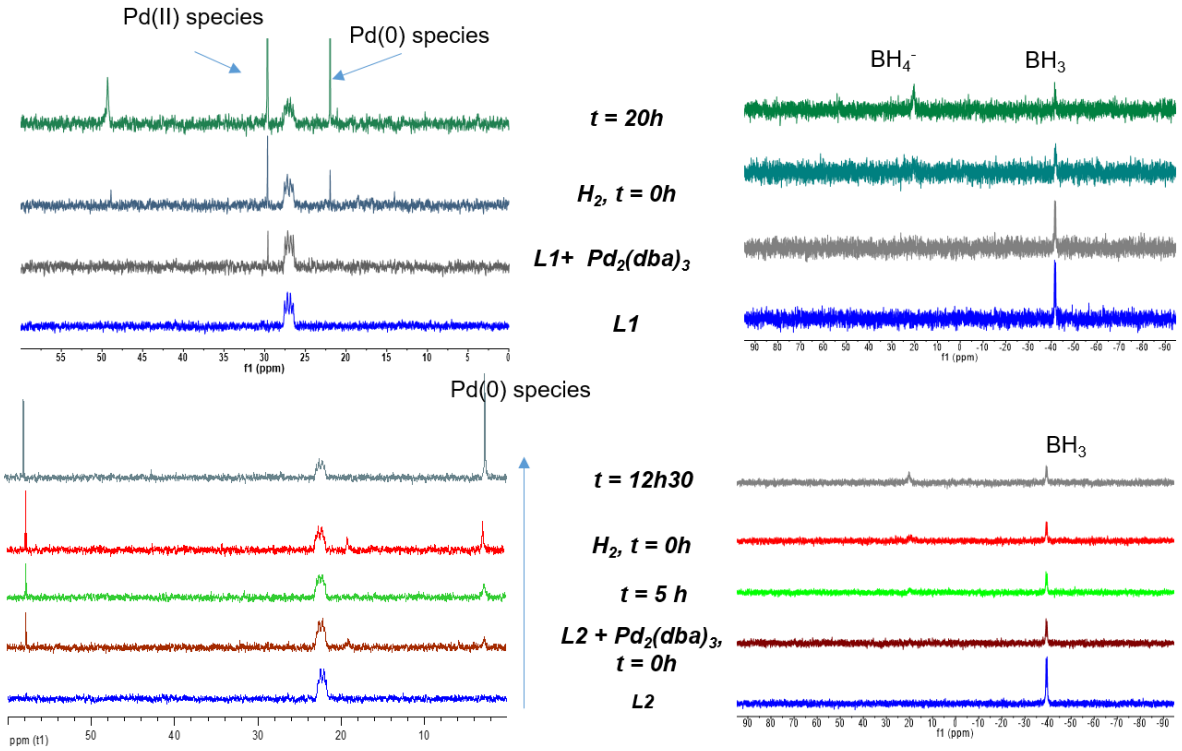


Figure S6. ^{31}P (162 MHz, solvent, 298 K) and ^{11}B (128 MHz, solvent, 298 K) NMR monitoring of the formation of **PdL1** (**top**) and **PdL2** (**bottom**).

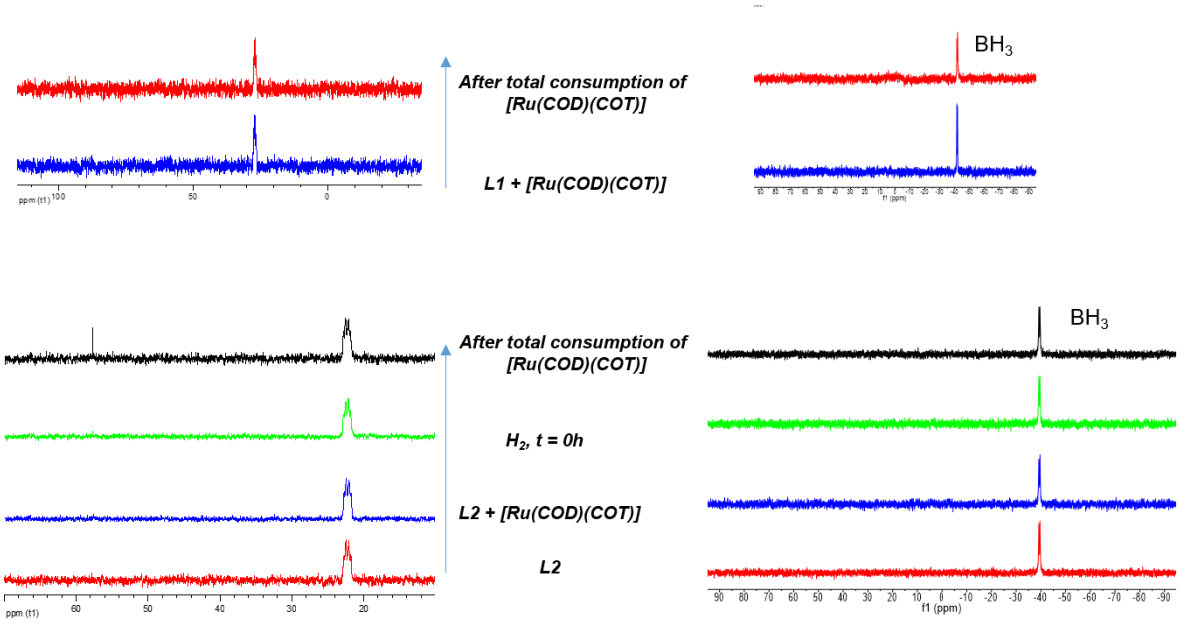


Figure S7. ^{31}P (162 MHz, solvent, 298 K) and ^{11}B (128 MHz, solvent, 298 K) NMR monitoring of the formation of **RuL1** and **RuL2**.

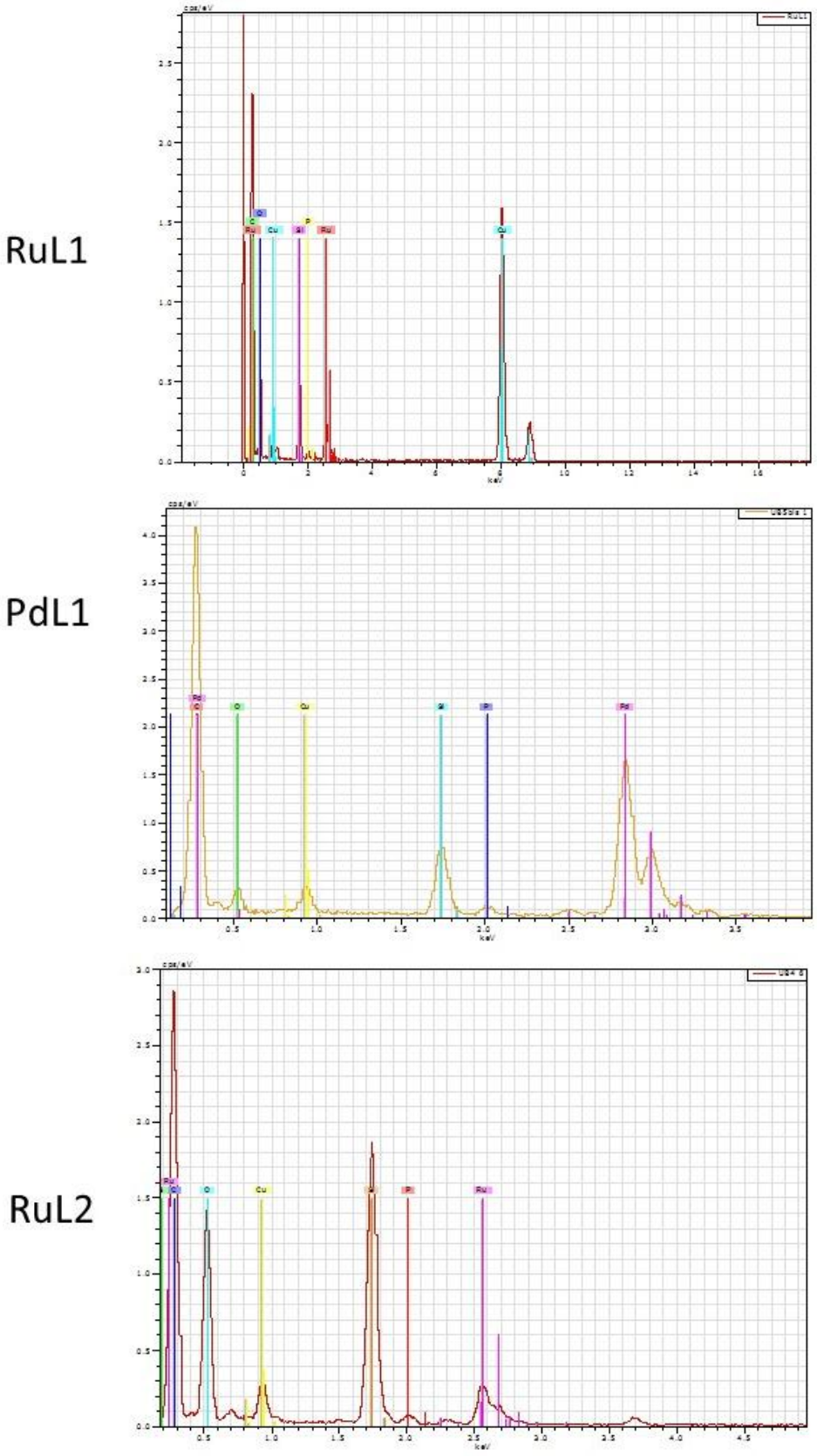


Figure S8. EDX (Energy Dispersive X-ray) analyses of **PdL1**, **RuL1** and **RuL2**.

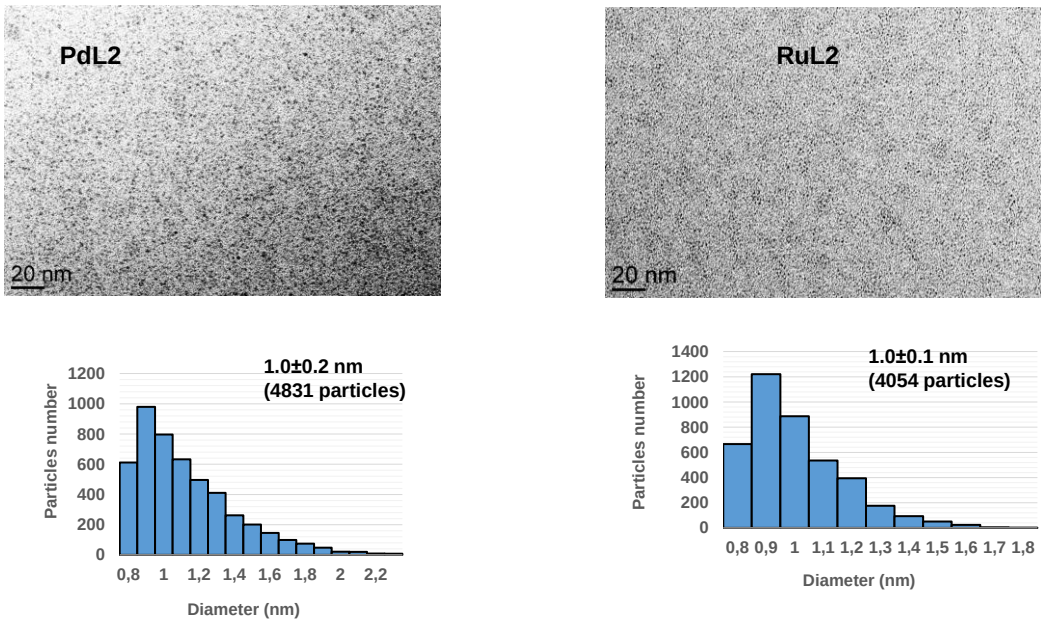


Figure S9. TEM (Transmission Electron Microscopy) isimages of **PdL2** and **RuL2** NPs stabilised with borane-free phosphine ligand, with the corresponding size distribution diagrams.

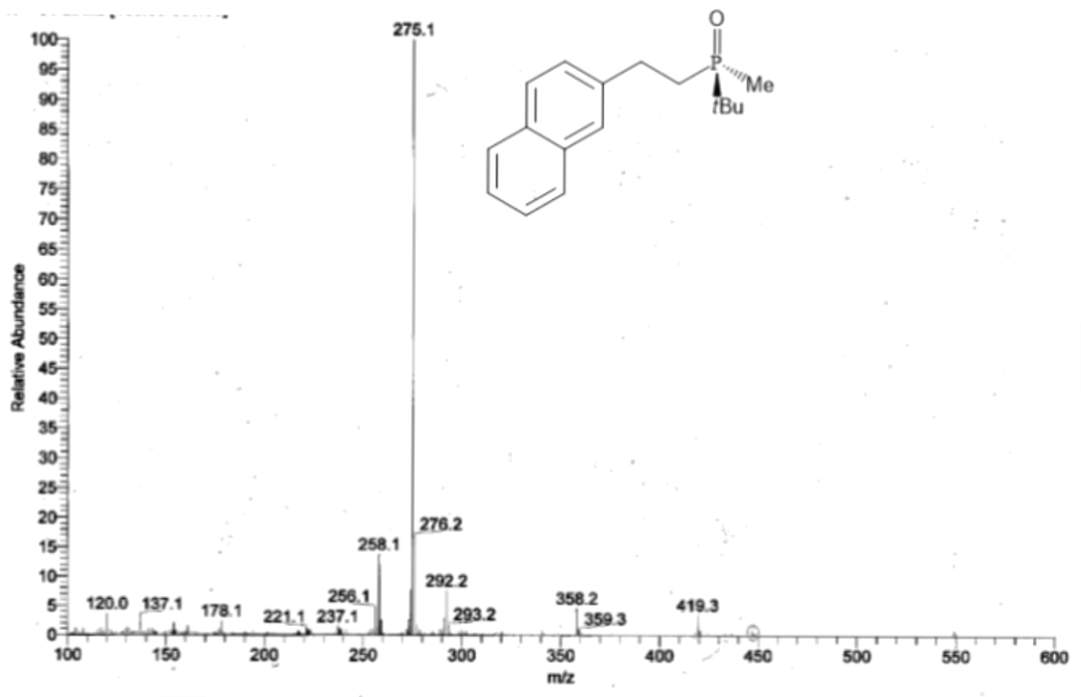


Figure S10. *Cont.*

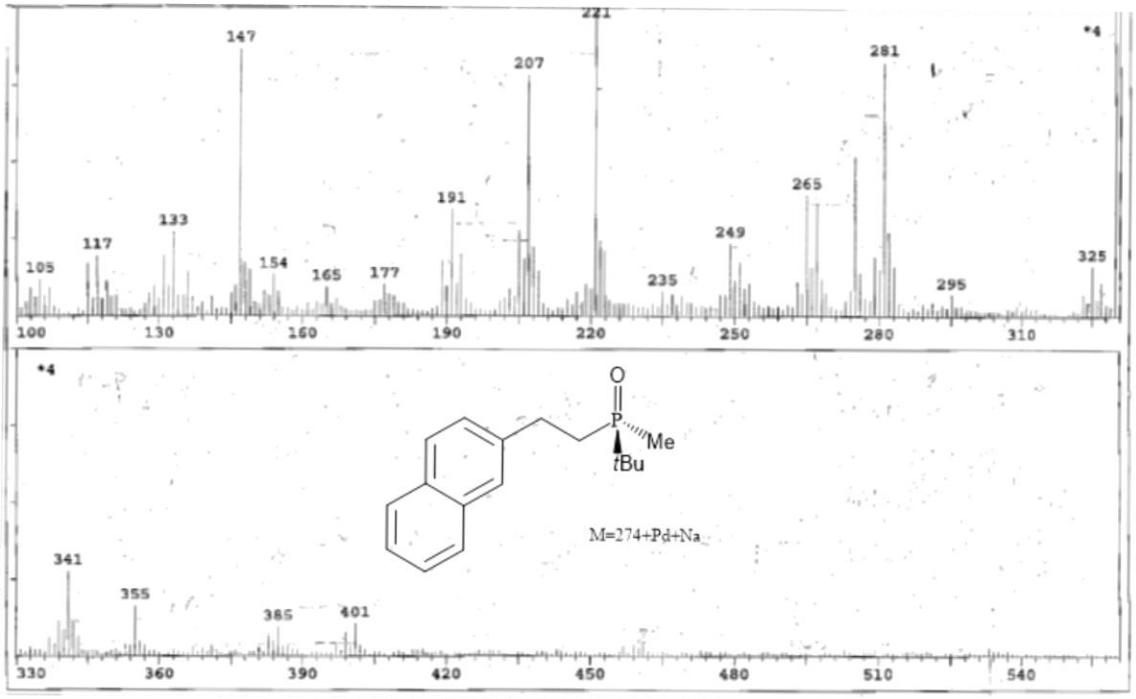


Figure S10. Mass spectrometry analyses of an organic phase of **PdL1** treated with H_2O_2(aq) and extracted with CH_2Cl_2 (FAB (**bottom**) and DCI/NH_3 analyses (**top**)).

For **PdL1**, we observed a peak at 275.1 corresponding to the borane-free phosphine (*M* = 258 g/mol) + NH_3 by DCI/NH_3 mass spectrometry and a peak at 401 corresponding to Pd(L1) + Na + O by FAB, which corresponds to the signal at +56 ppm in the ^{31}P NMR spectrum.

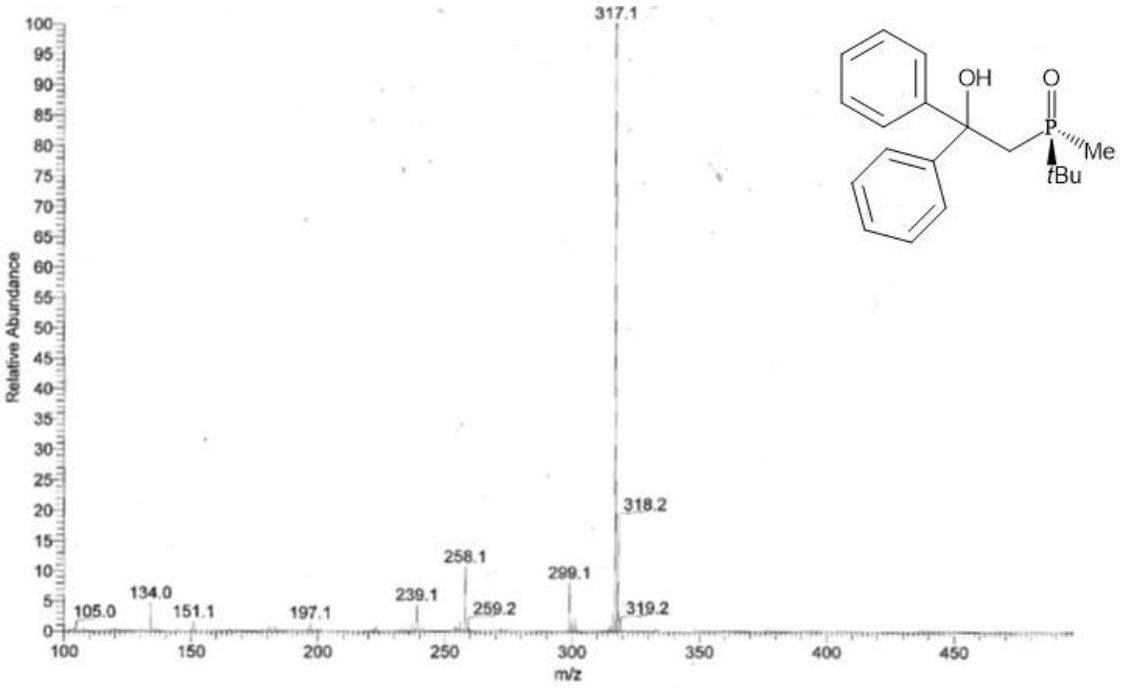


Figure S11. *Cont.*

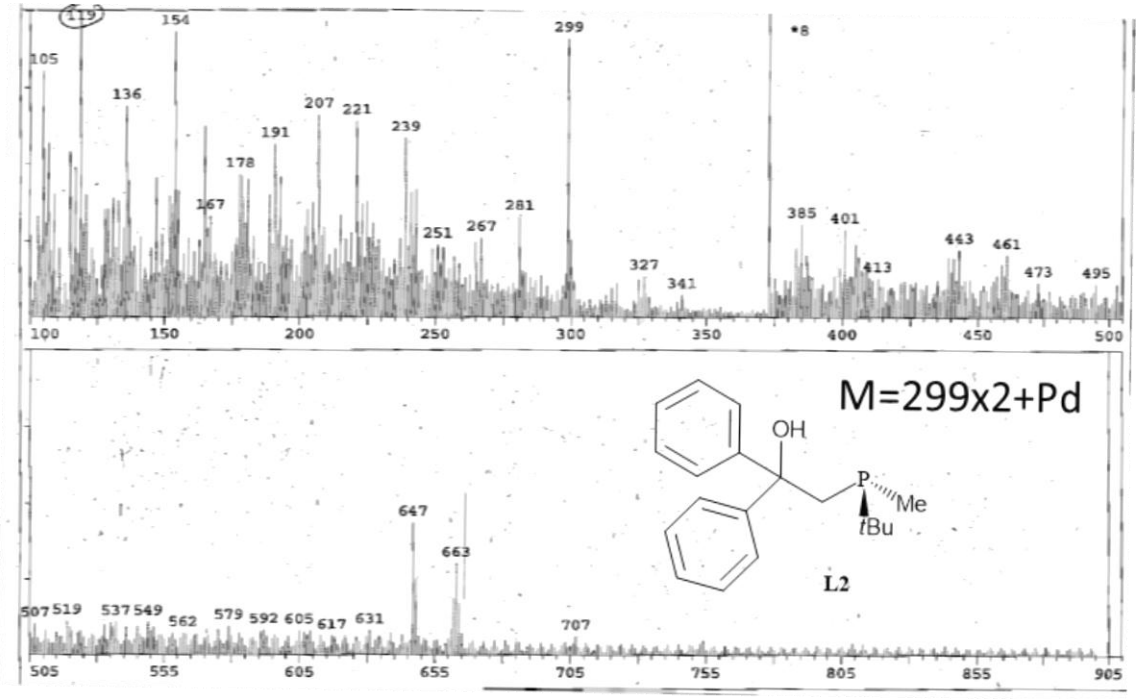


Figure S11. Mass spectrometry analyses of an organic phase of **PdL2** treated with H_2O_2(aq) and extracted with CH_2Cl_2 (FAB (**bottom**) and DCI/NH_3 analyses(**top**)).

For **PdL2**, we observed a peak at 317.1 corresponding to the borane-free phosphine **L2** (*M* = 299 g/mol) + NH_3 by DCI/NH_3 mass spectrometry and a peak at 707 corresponding to Pd(L2)2 by FAB, which corresponds to the signal at +60 ppm in the ^{31}P NMR spectrum.

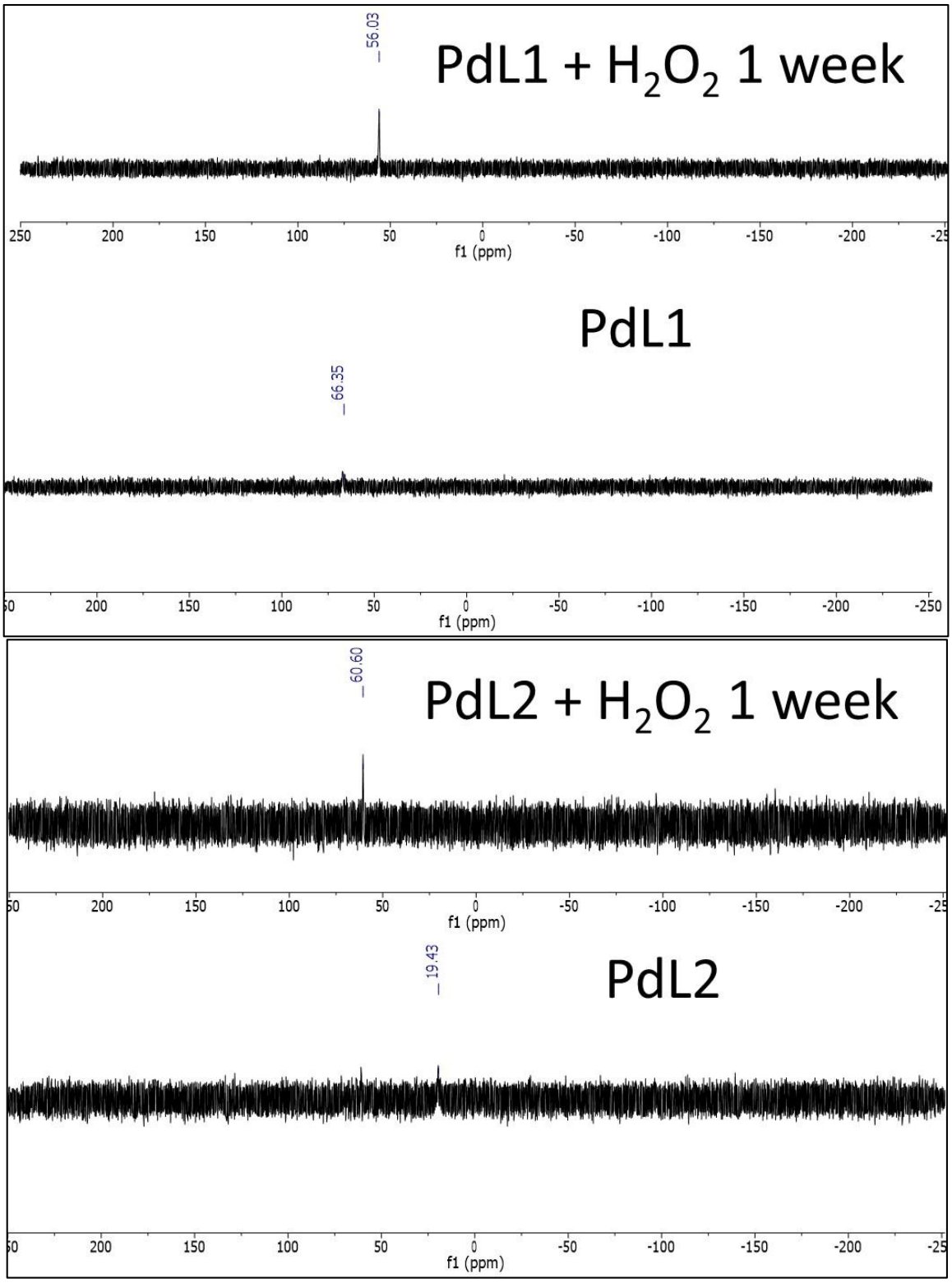
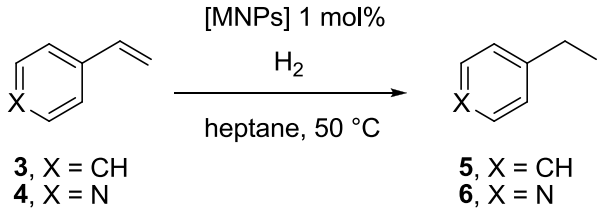


Figure S12. ^{31}P NMR spectra in $CDCl_3$ of PdNPs before and after addition of H_2O_2(aq).

Table S1. Hydrogenation of styrene and 4-vinylpyridine catalysed by **PdL** and **RuL** (**L** = **L1**, **L2**). [1]



3, X = CH
4, X = N

5, X = CH
6, X = N

MNPs = **PdL1**, **PdL2**, **RuL1**, **RuL2**

Entry	Catalyst	Substrate	H_2 Pressure (bar)	Time (h)	Conversion (%) [2]
1	**PdL1**	**3** or **4**	3	1	100
2	**PdL2**	**3** or **4**	3	1	100
3	**RuL1**	**3** or **4**	3	16	100
4	**RuL2**	**3** or **4**	3	16	100
5	**RuL1**	**3** or **4**	20	16	100
6	**RuL2**	**3** or **4**	20	16	100
7	**RuL2**	**3** or **4**	40	16	96 [3]
8	[Ru(COD)(COT)]	**3**	20	16	100 (64/36) [4]

[1] Reaction conditions: to form the metal nanoparticles: 5 mg of $[Pd_2(dba)_3]$ or 3 mg of [Ru(COD)(COT)] were mixed with 2 mg of ligand (**L1** or **L2**) in heptane at room temperature overnight under 3 bar of H_2. Then 1 mmol of substrate (4-Vinylpyridine (105 mg) or styrene (104 mg)) with 142 mg of decane as internal standard were added. Then the reaction was run at 50 °C for 1 to 16h under 3–40 bar H_2; [2] Determined by GC using decane as internal standard; [3] <5% of ethylcyclohexane or ethylpiperidine; [4] Mixture of ethylbenzene (64%) and ethylcyclohexane (36%).