

SUPPLEMENTARY MATERIAL

Figure S1. 2D ^{31}P NMR COSY spectrum of complex **1** in $\text{DMSO-}d_6$ at 318 K.

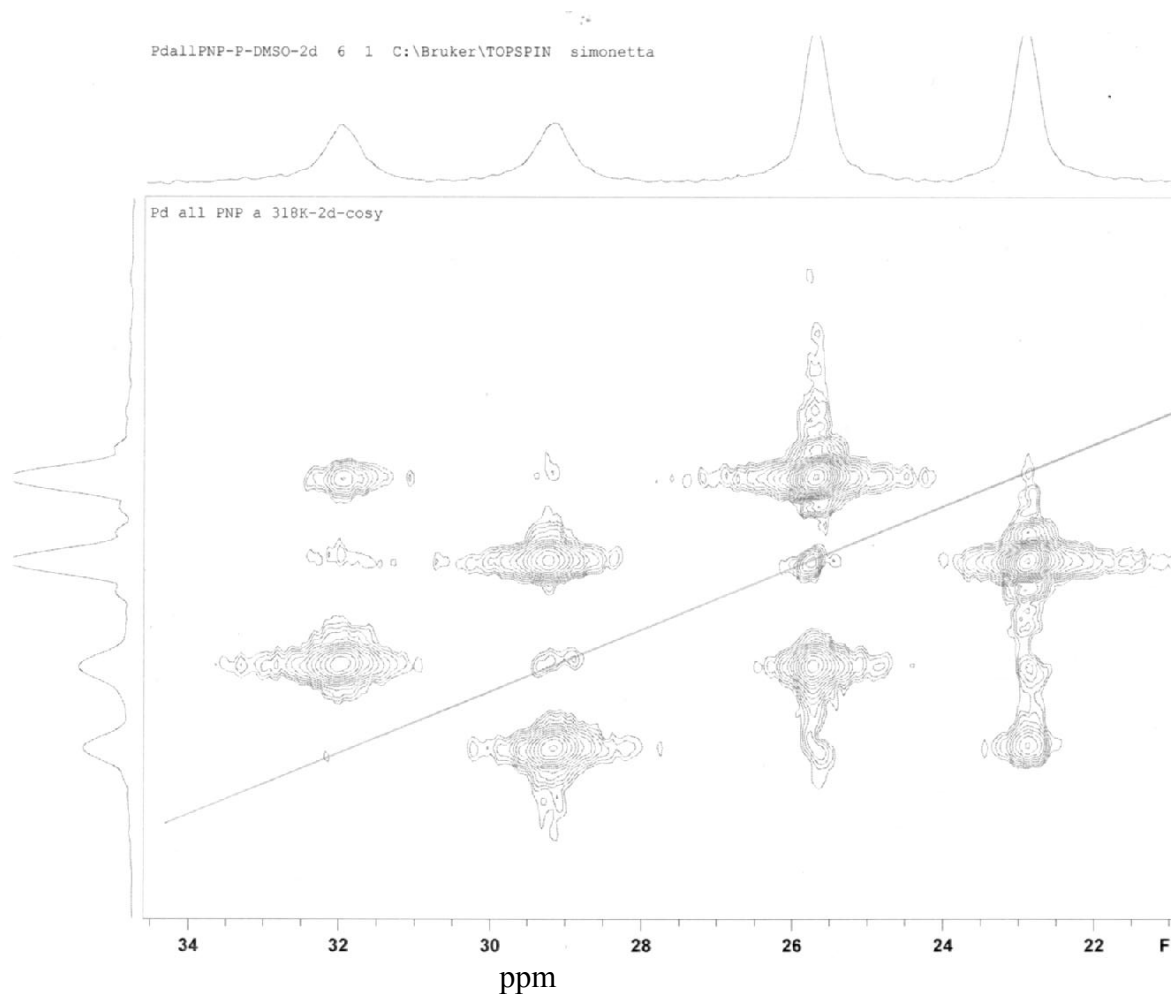


Table S1. Most significant geometrical parameters (Å, °) defining the coordination geometry of the palladium ion in complexes **3I**, **3II**, **4I** and **4II**, as derived from the fully geometry optimization of the model compounds.

Metal complex	3I	3II	4I	4II
Geometrical data				
Pd-P'	2.364	2.376	2.365	2.390
Pd-N	2.245	2.279	2.251	2.317
Pd-P''	2.369	2.427	2.372	2.452
Pd-CHR ¹	2.107	---	2.106	---
Pd-CH	---	---	---	---
Pd-CR ² R ³	---	2.145	---	2.160
P'-Pd-N	80.2	78.5	80.3	78.3
P'-Pd-P''	166.3	161.7	166.4	157.9
N-Pd-P''	86.4	83.6	86.6	80.2
P'-Pd-CHR ¹	96.4	---	96.9	---
P''-Pd-CHR ¹	97.0	---	96.2	---
N-Pd-CHR ¹	176.5	---	176.7	---
P'-Pd-CH	---	---	---	---
P''-Pd-CH	---	---	---	---
N-Pd-CH	---	---	---	---
P'-Pd-CR ² R ³	---	94.3	---	99.6
P''-Pd-CR ² R ³	---	103.8	---	102.1
N-Pd-CR ² R ³	---	172.0	---	176.3