

Supplementary Materials

Figure 1S. Homonuclear COSY spectrum of **1c**, in CD_2Cl_2 at 238 K (the *ortho* and *meta* protons of 4-picoline are evidenced).

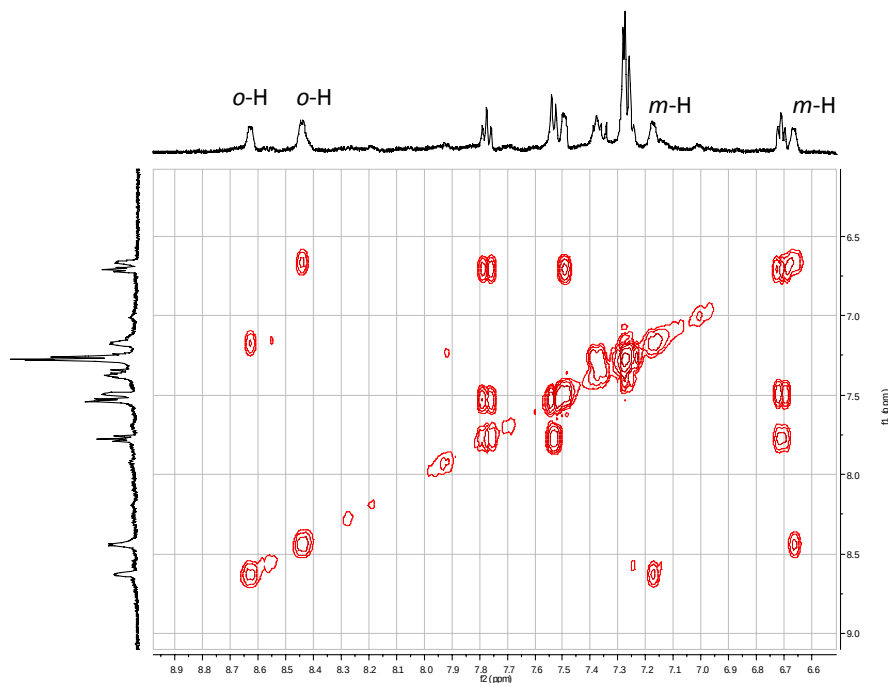


Figure 2S. NMR spectra of **1b**, in CD_2Cl_2 : variation with temperature (the *ortho*, *para* and *meta* protons of pyridine are evidenced).

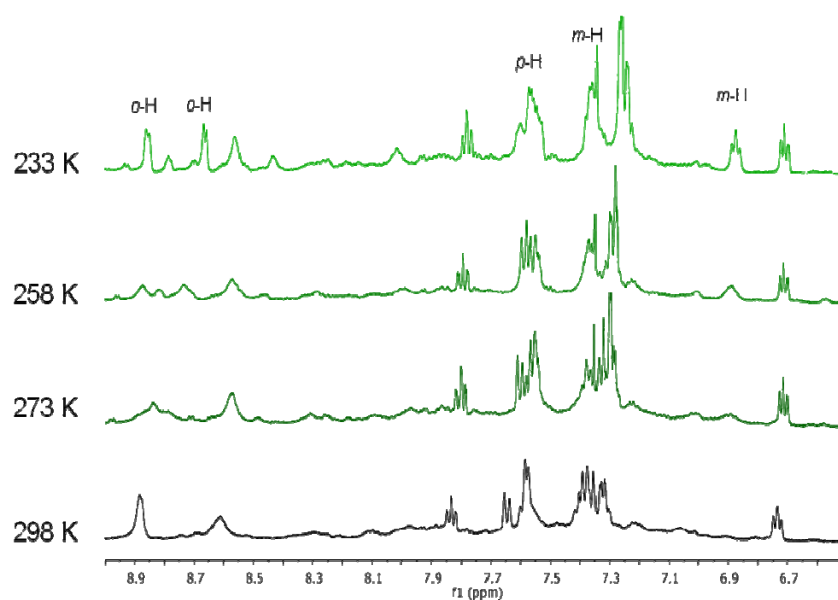


Figure 3S. Homonuclear COSY spectrum of **1b**, in CD_2Cl_2 at 233 K (the *ortho*, *para* and *meta* protons of pyridine are evidenced).

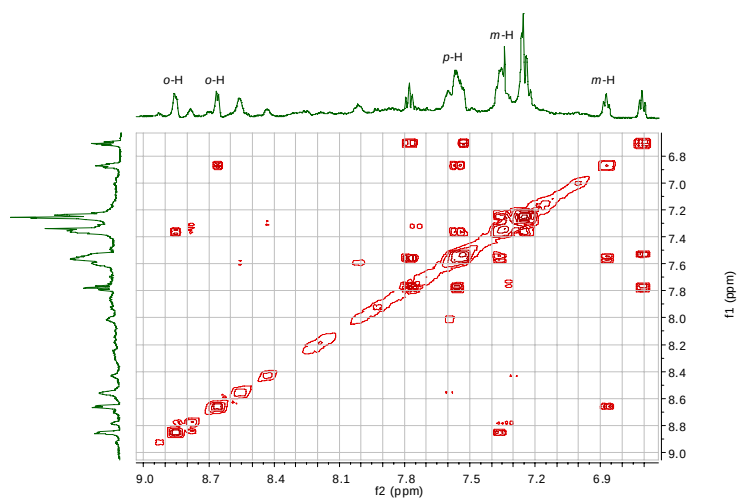


Figure 4S. NMR spectra of **1d**, in CD_2Cl_2 : variation with temperature (the *ortho* and *meta* protons of 4- CF_3 -pyridine are evidenced).

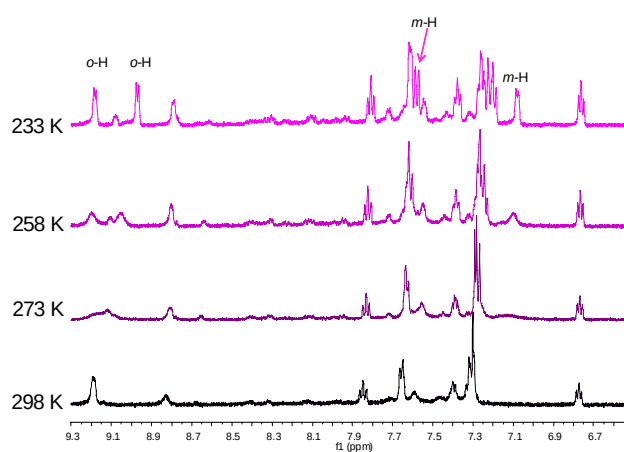


Figure 5S. Homonuclear COSY spectrum of **1d**, in CD_2Cl_2 at 238 K (the *ortho* and *meta* protons of 4- CF_3 -pyridine are evidenced).

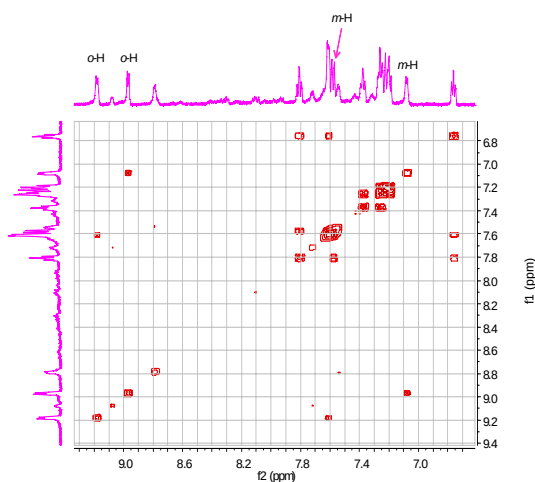


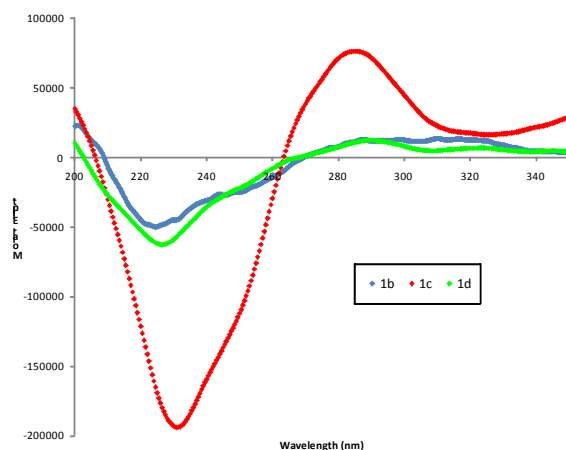
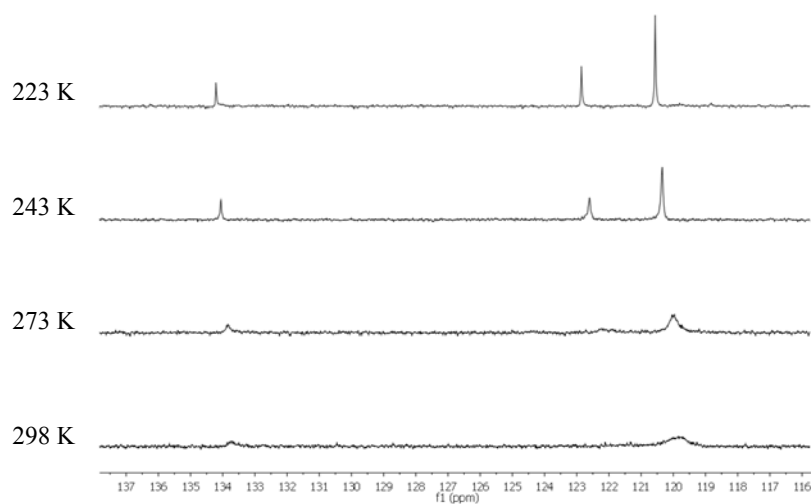
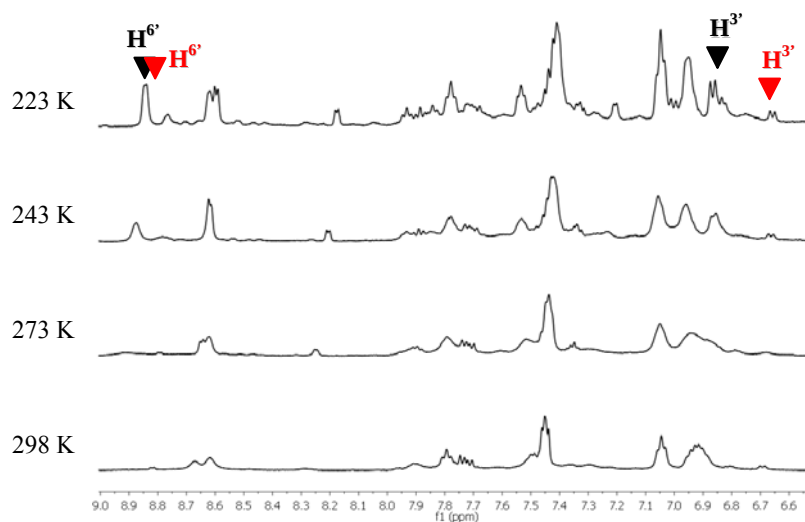
Figure 6S. CD spectra of complexes **1b-d** (1×10^{-4} M in CH₃OH).**Figure 7S.** ^{31}P - $\{^1\text{H}\}$ NMR spectra of **2b**, in CD₂Cl₂: variation with temperature.**Figure 8S.** ^1H NMR spectra of **2b**, in CD₂Cl₂ (aromatic region): variation with temperature (the *ortho* and *meta* protons of pyridine ring of P-N ligand are evidenced).

Figure 9S. ^1H NMR spectra of **2b**, in CD_2Cl_2 (portion of aliphatic region): variation with temperature (Pd- CH_3 groups are evidenced).

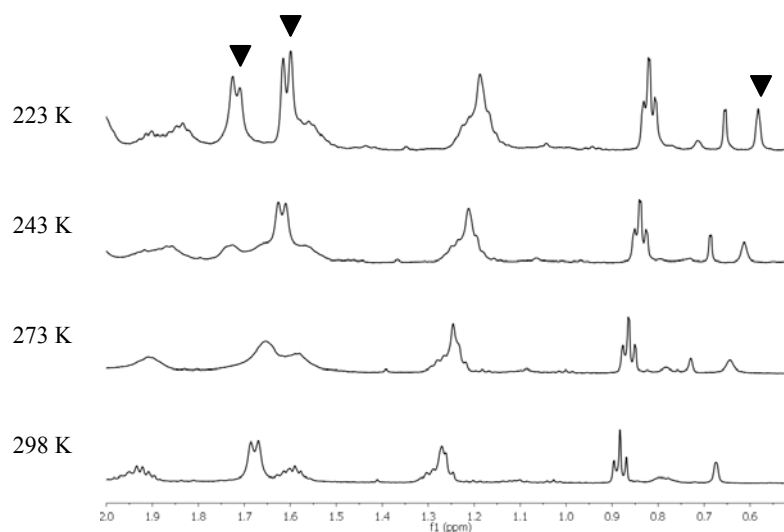


Figure 10S. ^1H , ^{31}P -HMBC NMR spectra of **2b**, in CD_2Cl_2 at 223 K.

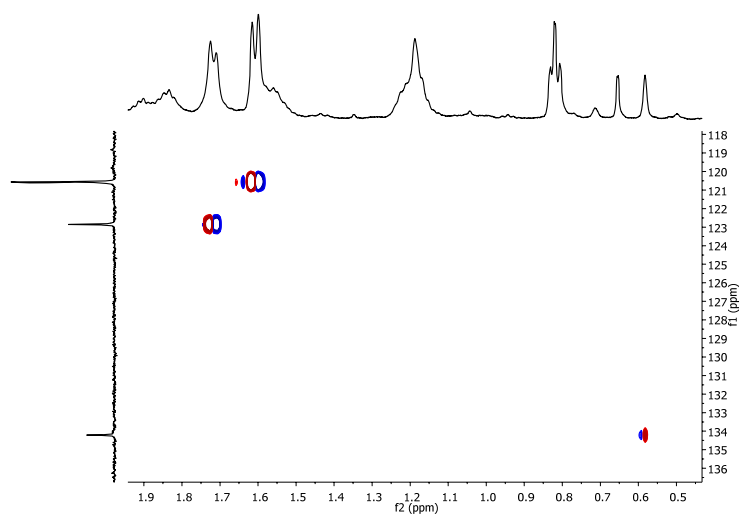


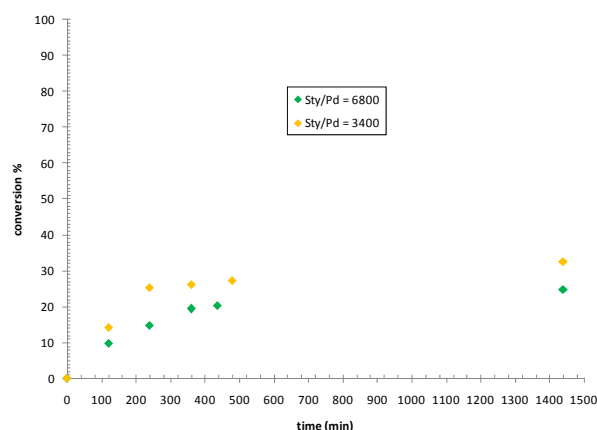
Table 1S. Selected coordination bond distances ($\text{\AA}$) for **1c**.

Pd(1)-N(1)	2.033(15)
Pd(1)-N(2)	2.131(13)
Pd(1)-N(7)	2.09(3)
Pd(1)-P(2)	2.224(10)
Pd(2)-N(5)	2.075(16)
Pd(2)-N(6)	2.095(13)
Pd(2)-N(3)	2.05(2)
Pd(2)-P(1)	2.208(13)

Table 2S. Styrene dimerization: effect of temperature. Precatalyst: **1c**.^a

Run	T (K)	TOF ^b	Conversion (%) ^c
1	303	9	8.81
2	323	67	16.70
3	343	159	24.83

^a Reaction conditions: $n_{\text{Pd}} = 1.27 \times 10^{-5}$ mol, $[\text{BQ}]/[\text{Pd}] = 40$, $[\text{styrene}]/[\text{Pd}] = 6800$, styrene $V = 10$ mL, TFE $V = 20$ mL; ^b Turnover frequency = moles of product obtained per mole of Pd after 2 h; ^c Conversion determined by HRGC analysis after 24 h.

Figure 11S. Styrene dimerization: effect of $[\text{styrene}]/[\text{Pd}]$. Precatalyst: **1c**.

Reaction conditions: see Table 2S, $n_{\text{Pd}} = 1.27 \times 10^{-5}$ mol for $[\text{styrene}]/[\text{Pd}] = 6800$, $n_{\text{Pd}} = 2.54 \times 10^{-5}$ mol for $[\text{styrene}]/[\text{Pd}] = 3400$, $T = 343$ K.

Table 3S. Styrene dimerization: effect of $[\text{BQ}]/[\text{Pd}]$. Precatalyst: **1b**.^a

Run	$[\text{BQ}]/[\text{Pd}]$	TOF ^b	Conversion (%) ^c
1	0	27	12.24
2	20	190	39.11
3	40	209	48.87
4	80	345	81.88

^a Reaction conditions: $n_{\text{Pd}} = 2.54 \times 10^{-5}$ mol, $[\text{styrene}]/[\text{Pd}] = 3400$, styrene $V = 10$ mL, TFE $V = 20$ mL; ^b Turnover frequency = moles of product obtained per mole of Pd after 2 h; ^c Conversion determined by HRGC analysis after 24 h.